ACCADEMIA DELLE SCIENZE
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ACCADEMIA NAZIONALE
DEI LINCEI

# ATTI
## DEL
# CONVEGNO MENDELEEVIANO

« PERIODICITÀ E SIMMETRIE
NELLA STRUTTURA ELEMENTARE
DELLA MATERIA »

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# PREFACE

*The present volume is a collection of papers presented in Turin and in Rome during the third week of September 1969.*

*They were prepared for an international conference celebrating the centennial of the discovery by Dimitri Ivanovich Mendeleev of the periodic system of the elements.*

*The topics covered in the different papers are for the most part centered upon the role that the notions of periodicity and symmetry have had and continue to have in chemistry as well as in atomic, nuclear and elementary particles physics.*

*The different contributions have been arranged according to an historical order. The papers dealing with atoms come first, then follow those dedicated to some aspects of nuclear dynamics and finally those dealing with the rich world of subnuclear particles.*

*By no means can it be said that the subject has been explored with a balanced treatment of its parts. The organizers of the conference, alone responsible for these shortcomings, were well aware of their difficult task. Yet, the masterful presentations of many viewpoints by the distinguished scholars who contributed to this volume represent a body of knowledge of lasting value and great interest.*

*May it serve to inspire creative thoughts for a better understanding of the eternal problem concerning the nature of matter.*

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## SALUTO DEL PROF. CARLO FERRARI
## PRESIDENTE DELL'ACCADEMIA DELLE SCIENZE DI TORINO

Ho il grande piacere e l'alto onore di rivolgere il saluto più cordiale agli insigni Scienziati qui convenuti per prendere parte al Convegno internazionale sul tema *Periodicità e simmetrie nella struttura elementare della materia* promosso da questa Accademia delle Scienze congiuntamente coll'Accademia Nazionale dei Lincei, per celebrare il centesimo anniversario della scoperta del sistema periodico degli elementi da parte di Mendeleev.

Dimitri Mendeleev fu Socio di questa Accademia: la fotografia, con firma in calce, nel biglietto d'invito a questa adunanza inaugurale del Convegno è la riproduzione della sua fotografia con autografo da lui inviata all'Accademia stessa. Purtroppo non siamo ancora riusciti a trovare nel ricchissimo epistolario di persone illustri esistente nella nostra biblioteca la corrispondenza con lui intercorsa.

La sua scoperta segna una data fondamentale nella storia delle Scienze fisiche e chimiche: da lungo tempo era stato intuito che le proprietà degli elementi chimici non sono distribuite a caso, ma con una certa regolarità in dipendenza della loro massa atomica, e si erano avute le leggi dal nome vagamente medioevale delle «triadi», da parte di Döhereiner nel 1817, della «vis tellurica» da parte di de Chancourtois nel 1862, e delle «ottave» da parte di Newlands nel 1863; ma fu soltanto nel 1869 che quello che era stato appena intuito ricevette la sua conferma definitiva con Mendeleev colla classificazione degli elementi che porta il suo nome: disponendo gli elementi per ordine di massa atomica crescente (oggi sappiamo che si deve dire per «numero atomico» crescente) egli ottenne un sistema in cui si hanno successioni (chiamate «periodi») di «elementi omologhi», cioè con proprietà fisiche e chimiche analoghe.

D'altra parte, la scoperta del sistema periodico doveva seguire quella dell'altra legge fondamentale che porta il nome del nostro Amedeo Avogadro: invero, è ben noto che il fatto che l'idrogeno sia biatomico fu riconosciuto precisamente coll'aiuto di detta legge, e che fino al 1850 la formula chimica dell'acqua era scritta HO. È vero che la legge di

Avogadro risale al 1811, ma sono note le vicissitudini attraverso alle quali essa passò prima di imporsi al mondo scientifico, così bene lumeggiate nella bella commemorazione tenuta da Eligio Perucca nel 1956.

È questo legame tra le due leggi che rende la sede di questa Accademia propria per la celebrazione del centenario della scoperta di Mendeleev: celebrazione non puramente storica, ma celebrazione più completa, che porta fino alla esposizione e alla discussione di quelli che sono stati gli sviluppi e i risultati più recenti che da detta scoperta sono derivati, o in qualche modo ad essa collegati. Già nel Simposio organizzato quest'anno dalla « American Chemical Society » appunto per la stessa commemorazione della nascita della Tabella Mendeleeviana, per la quale oggi siamo qui, Albert Ghiorso ha annunciato la scoperta dell'elemento sintetico (che non si trova cioè in natura, od almeno non si trova più, ma è creato dall'uomo) caratterizzato dal numero atomico 104 nella forma degli isotopi 257 e 259: questo, che è il più pesante degli elementi fino ad ora sintetizzati, e che si trova ben al di là dell'ultimo elemento della Tabella Mendeleeviana (il novantaduesimo, cioè l'Uranio), è il primo elemento della sezione del sistema periodico che Glenn T. Seaborg ha chiamato « regione transattinide ». Orbene: credo che risultati almeno altrettanto importanti saranno esposti e discussi in questo Convegno.

Ma il programma di questo non si arresta allo studio della struttura dell'atomo e delle proprietà chimiche, spettroscopiche con essa connesse, ma si spinge più addentro nella considerazione della struttura interna della materia, studiando le proprietà e le configurazioni dei nuclei atomici, e delle particelle elementari. Io non voglio e non posso entrare in un campo che non mi è familiare, ma dopo avere accennato alle ragioni e al carattere del Convegno, non posso non rispondere anche a quanto le persone non tanto interessate ai problemi scientifici quanto ai loro risultati, e forse anche preoccupate (e non senza ragione) per quello che Fisici e Chimici possono preparare coi loro studi alla umanità, legittimamente si domandano: a che servirà tutto questo? La risposta è: ad aumentare la conoscenza delle leggi fondamentali della natura. Questo è il fine principale, che trascende di gran lunga ogni applicazione specifica; queste per altro sono numerose, e fra quelle che già sono state fatte mi limiterò a ricordarne una, perché essa in qualche modo si collega ad un altro avvenimento che di recente ha sbigottito il mondo: nel 1967 la sonda spaziale Surveyor V eseguì un atterraggio morbido sulla luna e fece l'analisi chimica di materiali prelevati dalla superficie lunare impiegando una tecnica basata sull'irraggiamento del materiale da analizzare con particelle alfa: ora, la sorgente di queste particelle era il « curium 242 », uno di quegli elementi sintetici, al di là dell'Uranio nella Tabella di Mendeleev, cui prima ho fatto cenno.

Concludo queste mie poche parole rinnovando il saluto più cordiale a tutti e facendo i più vivi ringraziamenti alle Autorità qui presenti, ai relatori e a quanti parteciperanno alle discussioni per l'apporto che daranno alla buona riuscita dei lavori; un particolare ringraziamento ai Colleghi Wataghin e Verde che hanno curato con grande competenza e notevole impegno l'organizzazione tecnica del Convegno; e un particolare ringraziamento all'illustre prof. Beniamino Segre, Presidente della Accademia Nazionale dei Lincei, e alla Accademia Nazionale dei Lincei che colla loro adesione a promuovere insieme a noi questo Convegno hanno contribuito ad elevarne il prestigio. Ed infine, l'augurio più cordiale di buon lavoro.

## INDIRIZZO DEL PROF. BENIAMINO SEGRE PRESIDENTE DELL'ACCADEMIA NAZIONALE DEI LINCEI

*Autorità, cari Colleghi, Signore e Signori,*

È noto a tutti come la legge di Mendeleev — secondo cui le proprietà fisiche e chimiche degli elementi risultano una funzione periodica del peso atomico — sia oggi ancora una pietra angolare nello stupendo edificio della fisica e della chimica. Questa legge, intuita da A. de Chancourtois nel 1862 e da J. A. R. Newlands nel 1863, venne enunciata con pieno rigore logico e su basi sperimentali sicure da Dimitri Ivanovic Mendeleev in una prima fondamentale memoria pubblicata nel 1869 ed in un'altra definitiva uscita nel 1871.

Col presente Convegno internazionale celebriamo dunque il primo centenario di tale grande scoperta, con cui la chimica ha fatto un fondamentale salto di qualità, passando dal primitivo stadio imbevuto ancora di concezioni alchimistiche a quello odierno di scienza razionale. L'iniziativa del Convegno è stata presa congiuntamente dall'Accademia delle Scienze di Torino e dall'Accademia Nazionale dei Lincei, delle quali il Mendeleev fu uno dei Soci Stranieri più illustri: e la seconda di queste Accademie gelosamente conserva una lettera autografa di quest'ultimo, recante la data del 15/27 settembre 1893 e scritta nitidamente in italiano impeccabile, nella quale egli esprime la sua gratitudine per la nomina a Socio Linceo, accennando a « ... il più famoso chimico dei tempi nostri, il Signore Cannizzaro, i cui lavori mi furono sempre oggetto di ammirazione e di emulazione ».

È superfluo aggiungere che l'anelito verso un'interpretazione razionale del mondo fisico, attraverso alla ricerca ed allo studio di più o meno riposte e talora persino fantasiose armonie o simmetrie, sorse nell'uomo fin dalla più remota antichità. I Greci, ad esempio, denominavano simmetriche od asimmetriche due grandezze omogenee, per esprimere ch'esse rispettivamente ammettono o non ammettono una comune misura (il che si traduce oggi col dire ch'esse risultano fra loro commensurabili od incommensurabili); mentre poi, secondo Vitruvio, « La simmetria risulta dalla

proporzione, la quale è la commisurazione tra il tutto e le varie parti che lo costituiscono ».

La nozione di simmetria è venuta via via subendo un graduale processo di estensione ed affinamento, ampliandosi e precisandosi in quelle di periodicità e di permanenza od invarianza di fronte a mutamenti o trasformazioni di vario tipo; e non pare eccessivo l'asserire ch'essa sia stata e funga tuttora da principale elemento propulsore ed unificatore del sapere in rami basilari, che vanno dalla matematica alle scienze della natura, dalle arti alla filosofia.

Un Convegno di carattere interdisciplinare inteso ad illustrare e raffrontare i molteplici aspetti congeneri ed i collegamenti riguardanti le *Simmetrie* nei rami suddetti, è stato tenuto a Roma nel marzo scorso presso l'Accademia dei Lincei. Ad esso può idealmente venire ricongiunto il presente *Convegno mendeleeviano*, il quale — rifacendosi all'opera pionieristica del sommo chimico di Tobolsk, senza dimenticare quella precedentemente iniziata dal nostro Avogadro — si propone di approfondire gli sviluppi successivi, con particolare riguardo ai più recenti, riferentisi precisamente a *Periodicità e simmetrie nella struttura elementare della materia*.

Questo Convegno internazionale si articola in tre parti, di cui le prime due — relative a periodicità e simmetrie nell'atomo e nel nucleo — si svolgeranno qui a Torino, mentre la terza parte — dedicata a periodicità e simmetrie delle particelle elementari — si terrà a Roma presso l'Accademia Nazionale dei Lincei. Il denso programma si preannuncia così di enorme portata scientifica e grande attualità: ed io tengo a rinnovare i più sentiti ringraziamenti agli illustri studiosi italiani e stranieri che hanno accolto il nostro invito a svolgere una Relazione su uno dei suaccennati argomenti.

Mentre rivolgo un vivo ringraziamento alle Autorità qui presenti ed un caldo saluto a tutti i partecipanti, porgo a ciascuno di questi l'augurio di un piacevole e proficuo soggiorno prima in questa mia cara città natale o poi a Roma nell'ambito dell'Accademia che ho l'onore di presiedere, la quale può vantarsi di avere annoverato tra i propri Soci una pleiade di scienziati eminenti, da Galileo Galilei ad Enrico Fermi, e di averne pubblicati fondamentali contributi. E termino inneggiando alla cooperazione scientifica internazionale, sicuro fin d'ora del successo e della vasta eco che l'attuale Convegno susciterà nel mondo, fra i cultori dei più profondi studi di fisica e di chimica.

MARIO MILONE

# Da Avogadro a Mendeleev.

*Signore e Signori,*

da quando cessò di risuonare in questa Aula la voce di Amedeo Avogadro, direttore della Classe di Scienze F.M.N. (mancato il 9 luglio 1856) erano trascorsi soltanto pochi mesi, che già un altro scienziato italiano, un giovane siciliano, profugo politico nel Regno Sardo dal 1850, Stanislao Cannizzáro, professore di Chimica, prima al Collegio Nazionale di Alessandria e quindi all'Università di Genova, si apprestava con spirito acuto e battagliero a portare quel decisivo chiarimento, che determinò l'avvio all'adozione della teoria atomica unitaria.

Questa, pur essendo consequenziale alle ipotesi proposte da Avogadro sulla molecolarità dei corpi, era con esse rimasta in ombra per circa mezzo secolo a causa di artificiose barriere che, tenacemente mantenute anche dalle scuole più accreditate, costituirono in effetti gravi impedimenti al progredire della chimica nella prima metà del secolo scorso.

Proprio nel ripensare al modo di rendere, per il suo corso di insegnamento, più intuitiva e chiara l'esposizione dei principi della chimica e le valutazioni quantitative derivabili dalla considerazione delle reazioni chimiche, in chiave del principio di Avogadro, il Cannizzáro, attraverso alla pluriennale esperienza didattica, nel *Sunto di un corso di filosofia chimica* pubblicato sotto forma di lettera all'amico Salvatore De Luca nella primavera del 1858, giunge con sorprendente semplicità ed altrettanta precisione scientifica, a quelle definizioni chimiche di atomo e molecola, le quali sono ancora oggi alla base del nostro insegnamento nonchè al modo univoco di determinare, per via chimica, il peso atomico degli elementi.

Le stesse idee egli svolse poi al Congresso di Karlsrue nel 1860, alla presenza dei più noti chimici del tempo suscitando, anche attraverso accese polemiche, validi consensi alla formulazione di quella che fu poi chiamata *la legge degli atomi di Cannizzáro*. Alla riunione di Karlsrue sono presenti Lotar Meyer e Dimitri Mendeleev, i quali ricevono il *seme*, lanciato da Cannizzáro: e questo seme germogliando in terreni già pre-

parati e particolarmente fertili, in breve fruttificherà con le proposte di *classificazione degli elementi* esposte dal Meyer nel 1864 e da Mendeleev nel 1869.

Scrisse infatti il Meyer: «... fui colpito dalla chiarezza che questo piccolo scritto (il *Sunto* distribuito ai congressisti di Karlsrue) emanava sulle questioni più importanti. Ciò mi schiarì la vista, mi fece cadere i dubbi ed ebbi la sensazione di una tranquilla certezza. Se alcuni anni più tardi ho potuto contribuire a chiarire questo soggetto... lo debbo in gran parte allo studio di Cannizzáro ».

Espressioni del tutto anologhe furono usate dal Mendeleev nel suo resoconto sul Congresso.

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A veder bene non si può dire che fino a quei tempi in Italia fossero esistite scuole di chimica, da mettere a confronto con le ormai numerose francesi, tedesche, inglesi, scandinave dove legioni di chimici, seppure spesso discordi fra di loro, avviavano faticosamente la chimica verso un piano più scientifico e unitario.

Così pure a Torino, fino a quando non vi fu chiamato nel 1855 dall'Università di Pisa Raffaele Piria, che effettivamente fondò un vivaio di studiosi, i quali in seguito ebbero a distinguersi.

Si erano bensì formati a Torino alcuni buoni cultori della chimica: ricordiamo *Claudio Berthollet*, che migrato in Francia fu maestro di Gay Lussac e assunse a notorietà non solo perché continuatore dell'opera di Lavoisier, ma anche per applicazioni pratiche da lui ottenute; *Giovanni Antonio Giobert*, attento analista; *Ascanio Sobrero*, preciso preparatore di nuovi composti organici (a lui si deve tra l'altro la preparazione della nitroglicerina!); *Francesco Selmi*, noto per le sue ricerche: in tossicologia (scoprì le ptomaine dei cadaveri), in biochimica e in quella che fu poi la chimica colloidale.

Essi seppero sopperire con l'ingegno e l'industriosità sperimentale alla inadeguatezza dei mezzi conseguente all'incertezza dei tempi, alle guerre, alle lotte politiche e alle incomprensioni derivantine e che fatalmente favorivano quella tendenza all'isolamentismo, notoriamente connaturata nel carattere pedemontano.

Tuttavia pur nella carenza spirituale e materiale dell'ambiente, il *fisico* Amedeo Avogadro, che però pensava e sperimentava molto anche di chimica, professore di filosofia positiva nel Collegio (Liceo) di Vercelli, nel 1811 espone con il « *Saggio di un modo di determinare le masse relative delle molecole elementari dei corpi e le proporzioni secondo le quali esse entrano in queste combinazioni* », quella immortale ipotesi che tuttora è

il punto di partenza di ogni ragionamento chimico fisico: anche se rimase praticamente non considerata dai contemporanei. E questo non perché sconosciuta (fu difatti pubblicata in periodici francesi di larga diffusione) ma perché non rientrava negli schemi e nelle regole tradizionali sui quali i più noti capiscuola della chimica (Dalton, Berzelius, Dumas, Gmelin, ecc.) perduravano con autoritarismo a impegnare il loro prestigio personale: e neppure sono da escludere motivi politici e nazionalistici.

Il riconoscimento dei chimici venne all'Avogadro solo attraverso l'opera di Cannizzáro, ma ben più tardivo gli venne dai fisici anche se, come ricordò il nostro Perucca nella magistrale rievocazione tenuta in commemorazione del centenario della morte: «non era ancora asciutta la calce della tomba di Quaregna, quando esplose, ad opera di Krönig, la *teoria cinetica*», che delle ipotesi di Avogadro costituisce ancora convincente dimostrazione teorica.

È infatti ben noto che molte delle idee che compaiono nel corso di ricerche scientifiche hanno una storia di alterne vicende e non assumono una forma determinata se non gradualmente.

Sovente esse non vengono riconosciute senza prima aver trovato una certa resistenza, tanto più tenace quanto più sono antitradizionalistiche, e spesso riescono ad imporsi solo quando gli avversari scompaiono dalla scena e la nuova generazione acquista fin dall'inizio familiarità con le nuove idee.

È altresì noto che generalmente le scoperte scientifiche, grandi o piccole, risultano da una catena continua di osservazioni collettive, di ragionamenti e di deduzioni dalle esperienze, per cui riesce spesso impossibile di rintracciare la genesi d'una scoperta e di attribuirle una precisa paternità. Ma talvolta è proprio la geniale intuizione del singolo che segna la svolta decisiva verso nuove vie nella evolventesi conoscenza di un problema scientifico naturale.

Tali avvenimenti, che diventano possibili solo quando i tempi sono maturi, risultano ben identificabili.

Sarà forse esagerato affermare, come fece Bunsen, che la chimica moderna prende l'avvio dall'ipotesi di Avogadro: ma è certo che fu l'Avogadro a darci il modo di pervenire a complete ed esatte informazioni sull'esistenza, sulla individualità, sull'uniformità per ogni specie chimica delle *particelle elementari* (molecole ed atomi) di cui sono formati gli individui chimici e sulle loro proprietà chimico fisiche.

Ai tempi di Avogadro la sperimentazione chimica era diretta a proplemi di preparazione e di analisi: ma ci si cincischiava sui risultati numerici empiricamente ottenuti, limitandosi ad evidenziare e confermare i rapporti *di equivalenza* relativa nella combinazione degli elementi per la formazione dei composti.

Quella che sarà poi la *legge molecolare di Avogadro* nasceva, invece per felice intuizione, dalla attenta considerazione stechiometrica dei *risultati chimici* delle esperienze di Gay Lussac sui gas. L'Avogadro infatti sulla base dei pesi molecolari così calcolabili mette in chiaro la differenza tra molecole ed atomi, riconoscendo l'esistenza di *molecole integranti* (termine derivato da Haüy, fondatore della cristallografia, indicante le molecole dei composti nell'attuale nostro significato) di *molecole costituenti* (molecole formate da atomi uguali, cioè molecole di elementi) di *molecole elementari* o *semplici* (i nostri atomi).

Sulla base di questi enunciati e sulla scorta della vasta sperimentazione analitica e pertanto in un ambiente che andava rapidamente maturando, Cannizzáro con spirito veramente galileiano (analisi del fenomeno naturale per mezzo delle relazioni quantitative) può indicare la via alla *legge degli atomi* facendo constatare che i *pesi molecolari* corrispondono pure stechiometricamente alla somma dei *pesi atomici* degli atomi combinati, e questi *pesi atomici* sono caratteristici degli atomi degli elementi chimici e non chimicamente suscettibili di suddivisione.

È proprio da questa sicura scala ponderale che permetteva di definire i singoli elementi, di coordinarli e di confrontarli, sùlla base di correlazioni chimiche e fisiche che prese l'avvio il Mendeleev per dettare la *legge della periodicità* e costruire il suo sistema periodico.

Lo affermò egli stesso più volte e ancora nella Faraday Lecture letta nell'Anfiteatro della Royal Institution il 4 giugno 1889, riferendosi al congresso di Karlsrue — «... le idee di Cannizzáro provarono di essere le sole che potevano resistere alla critica e che rappresentavano l'atomo come la più piccola porzione di un elemento che entra nella molecola dei suoi composti. Solo questo reale peso atomico può fornire una base per generalizzazioni — ».

E altrettanto probanti sono le dichiarazioni dello stesso raccolte dal figlio: « io considero il Cannizzáro come un mio precursore, poiché i pesi atomici da lui stabiliti, mi hanno fornito il necessario punto d'appoggio ».

Fino a quando non fu enunciato il pur semplice principio di Cannizzáro, non poteva avere successo una correlazione anche soltanto a scopo didattico, tra le proprietà chimico fisiche degli elementi chimici, perché veniva a mancare la base di riferimento: e quindi non stupisce l'insuccesso dei numerosi precedenti tentativi di sistematica in chimica inorganica.

Non credo sia qui fuori luogo ricordare che anche il *chimico* Amedeo Avogadro, avendo fin dal 1814 dimostrato la formula $SiO_2$ per la silice, in seguito, e per confronto analogico attribuì, in netto disaccordo con quanto sostenevano invece i grandi della chimica contemporanei, la for-

mulazione $AO_2$ per le anidridi del carbonio, dello stagno, del titanio, dello zirconio e la formula $ACl_4$ per i rispettivi cloruri, cioè aveva *chimicamente caratterizzato* gli elementi del IV gruppo del sistema periodico mendeleviano assai prima che detto sistema venisse elaborato e proposto.

Le cronache narrano che neanche i chimici e i fisici italiani e in particolare quei pochi che operarono a Torino, pur avendo l'Avogadro insistito sul suo principio in numerose note presentate a questa Accademia, avevano percepito la grande verità contenuta nell'opera geniale dei due grandi novatori: così lo stesso Piria, maestro di Cannizzáro, e che resta certamente tra i maggiori chimici che insegnarono nelle Università italiane (talché il busto nella nostra Università, inaugurato solennemente nel 1883 con un'orazione di Cannizzáro, fu eretto per *sottoscrizione nazionale*).

Il Piria, che continuava ad insegnare la chimica barcamenandosi tra le vecchie e nuove teorie, ancora negli ultimi mesi di vita (morì a Torino nel 1865) si dichiarava dubbioso sulla vessata questione: equivalenza e teoria atomica.

Tuttavia non è azzardato attribuire alla presenza nell'ambiente torinese (il Cannizzáro si recava e soggiornava spesso a Torino anche per ragioni politiche: tra l'altro fu promotore e propugnatore presso il Governo piemontese della chiamata di Piria a Torino) e agli inevitabili contatti con l'Avogadro anche nell'ambito della nostra Accademia, una decisa influenza sul sorgere dell'idea direttrice della legge atomica di Cannizzáro, che proprio in quel tempo si sviluppò nella mente del giovane Siciliano per le necessità del suo insegnamento.

Pure l'apparizione delle comunicazioni di Mendeleev sulla legge periodica non provocò un particolare e diretto interessamento nell'ambiente dei chimici, forse perché i chimici di allora erano ancora impegnati a fondo nel lavoro preparativo, a collezionare e ricercare fatti, piuttosto che meditare sulle relazioni tra questi, ma anche perché la caducità di altri tentativi di classificazione aveva suscitato negli studiosi un atteggiamento di netto scetticismo nei riguardi di nuovi tentativi di generalizzazione.

Vi furono critiche e obbiezioni che perdurarono anche dopo la scoperta di quegli elementi preconizzati dal Mendeleev nei dettagli delle loro proprietà chimiche e fisiche: proprio per quella isteresi intellettuale esistente purtroppo anche in molti uomini di scienza. Così in Italia, mentre alcuni allievi della scuola romana di Cannizzáro, tra i quali in primis il Piccini, riuscivano a portare alcune interessanti integrazioni necessarie alla classificazione, questa in altre sedi veniva praticamente ignorata: e proprio qui a Torino gli studenti in chimica ancora negli anni venti si laureavano senza esserne edotti.

E pensare che tanto Cannizzáro quanto Mendeleev furono spinti l'uno al consolidamento della teoria atomica, l'altro al coordinamento delle correlazioni tra le proprietà chimico fisiche degli elementi chimici, proprio nel tentativo di razionalizzare l'insegnamento della chimica e renderlo più accettabile agli studenti. In particolare la chimica inorganica veniva a cessare di essere una nuda esposizione di fatti incoerenti da memoralizzare come vocaboli per lo studio di una nuova lingua, dato che il sistema periodico ne forniva invece una regolamentazione pianificata che dava significato alle vecchie acquisizioni e ne preveniva altre nuove.

Praticamente la teoria della valenza, che era già stata intravista dal Cannizzáro, nel suo «Sunto» trova nella sistematica mendeleeviana una naturale giustificazione e un proficuo sviluppo e le deduzioni teorico-strutturali deducibili dalle ricerche spettrografiche e poi dimostrate dalla chimica nucleare, risultano inquadrarsi nel quadro periodico.

La concezione di Mendeleev difatti costituisce proprio una *legge quadro* (per usare la dizione oggi molto alla moda) nella quale, essendo stati affermati alcuni limiti e condizioni, furono saggiamente previste lacune, ove sistemare le nuove accessioni e anche spostamenti, che la scoperta degli *isotopi* ha in seguito pienamente sanzionato.

È invero sorprendente che

le *leggi delle molecole*

le *leggi degli atomi*

le *leggi della periodicità*

le quali interpretano il comportamento chimico fisico quali-quantitativo di atomi e molecole, alla cui enunciazione si era giunti in modo unicamente empirico, abbiano ricevuto piena giustificazione e interpretazione dalle attuali conoscenze teoriche sulla struttura elettronica dell'atomo, sul legame chimico, sulla meccanica e dinamica dei nuclei (*leggi nucleari*) non assolutamente prevedibili dalla chimica e dalla fisica di un secolo fa.

L'attuale riunione commemorativa non può non essere considerata come un'ideale continuazione di quella altrettanto solenne, tenuta a Roma nel dicembre 1960, organizzata sotto l'egida della Società Chimica Italiana e dell'Accademia Nazionale dei XL, da Domenico Marotta che di esse era rispettivamente Presidente e Segretario Generale, e dedicata alla rievocazione del centenario del Congresso di Karlsrue.

Nel corso di essa Michele Giua, Alexander Todd, George Chaudron e Nicolav Alexandrovic Tigurovski ricordarono che quel memorabile convegno scientifico determinò l'avvio verso un nuovo e più razionale indirizzo di impostazioni del pensiero chimico.

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In particolare l'oratore russo rievocando la feconda amicizia che si strinse in quella occasione tra Mendeleev e Cannizzáro riaffermò l'evidenza che:

« l'ammirevole intervento (di Cannizzáro) ha segnato una tappa fondamentale nella storia della chimica ed ha contribuito al progresso delle teorie chimiche, anticipando la scoperta della legge periodica di Dimitri Mendeleev ».

Ho oltrepassato i limiti di tempo predisposti dal programma: spero che però vorrete giustificare il chimico torinese che si è attardato non dico a rivendicare, ma soltanto a richiamare la vostra attenzione sull'importanza euristica ed epistemologica di fatti che sulla via verso la grande scoperta di Mendeleev si sono qui svolti.

Icilio Guareschi, illustre storico della Chimica, professore per quarant'anni nella nostra Università, in una sua nota nei nostri Atti Accademici del 1916 ha diagrammato nella serie

Dalton → Avogadro → Gerhardt → Cannizzáro → Mendeleev

i principali protagonisti di vicende scientifiche, attraverso i quali è passato il filo conduttore che ha portato alle nostre attuali conoscenze sulle proprietà chimico fisiche degli atomi in dipendenza della loro struttura.

Oggi, a ragione meglio ponderata, mi permetterei aggiungere all'inizio della serie il nome di Gay Lussac, che va senz'altro ritenuto il fondatore dellla stechiochimica, e alla fine quello di Enrico Fermi, che con il suo valido contributo teorico e sperimentale alla caratterizzazione del neutrone e delle reazioni nucleari (leggi nucleari) ha permesso la dimostrazione chimico-strutturale della sistematica degli elementi proposta da Mendeleev: quel filo conduttore cui ha or ora accennato il collega Spitzin pertanto è passato più volte per l'Italia e due volte per il Piemonte, pronuba la nostra Accademia.

L'opera espressa dal genio di Mendeleev, proprio a piena maturità dei tempi, ha suscitato crescente ammirazione ed ha raggiunto pieno riconoscimento nel corso di questi cento anni e anzi, come abbiamo appreso dalla documentata orazione del collega russo che mi ha preceduto, con il progredire delle conoscenze scientifiche non solo ha mantenuta integra la sua vitalità e validità, ma le ha viste esaltare: sicché non è azzardato ritenere che il *Sistema Periodico* di *Mendeleev* nella mente degli uomini di scienza, di studio e di lavoro durerà indelebile nei secoli, per certo assai più a lungo che non quello inciso sulla pietra, che nel Cimitero di Wolkovo, ricopre le spoglie mortali di Dimitri Mendeleev.

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V. I. SPITSYNE (*)

# Le centenaire de la loi périodique de Mendéléev.

Il y a cent ans, au début de mars 1869, D. I. Mendéléev, alors professeur de chimie à l'Université de Saint-Pétersbourg, fit parvenir à de nombreux savants russes et étrangers un feuillet représentant le Système des élements élaboré par lui.

Ce système avait été fondé sur les poids atomiques et les similitudes chimiques des éléments (fig. 1).

A la séance du 18 mars 1869 de la Société chimique de Russie Mendéléev fit une conférence sur ce travail. Au mois de mai de la même année il publia dans le fascicule courant de la Revue de la Société chimique de Russie [1] son mémoire « La relation entre les propriétés des éléments et leurs poids atomiques ». Il y a donné cette première expression de la loi périodique: « Les éléments disposés par ordre de leurs poids atomiques manifestent une périodicité nette de leurs propriétés ». Quelques années plus tard Mendéléev a donné l'expression suivante plus précise encore de la loi périodique: « Les propriétés des corps simples ainsi que les formes et les propriétés des composés chimiques des éléments montrent la dépendance périodique de leurs poids atomiques ».

La découverte de la loi périodique et du système naturel des éléments chimiques qui y était lié résultait des travaux de Mendéléev sur son œuvre « Les fondements de la chimie », traité célèbre de chimie minérale qu'il a commencé à rédiger en 1868 ». Ce livre contient beaucoup de matières originales..., mais surtout la périodicité des éléments qui a été justement découverte au cours de la rédaction des « Fondements de la chimie », indiquait plus tard Mendéléev [2].

On sait que des tentatives de classer les éléments, de les répartir en groupes et en tableaux ont été faites avant Mendéléev. On peut citer à ce propos les triades de Döbereiner — Ca, Sr, Ba; S, Se, Te etc. (1829) auxquelles ont succédé les groupes de Pettenkofer (1850) — N, P, As, Sb; Mg, Ca, Sr, Ba etc., la Spirale de Chancourtois (1862), les tableaux

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# ESSAI D'UNE SYSTÈME DES ÉLÉMENTS

## D'APRES LEURS POIDS ATOMIQUES ET FONCTIONS CHIMIQUES,

### par D. Mendeleeff,

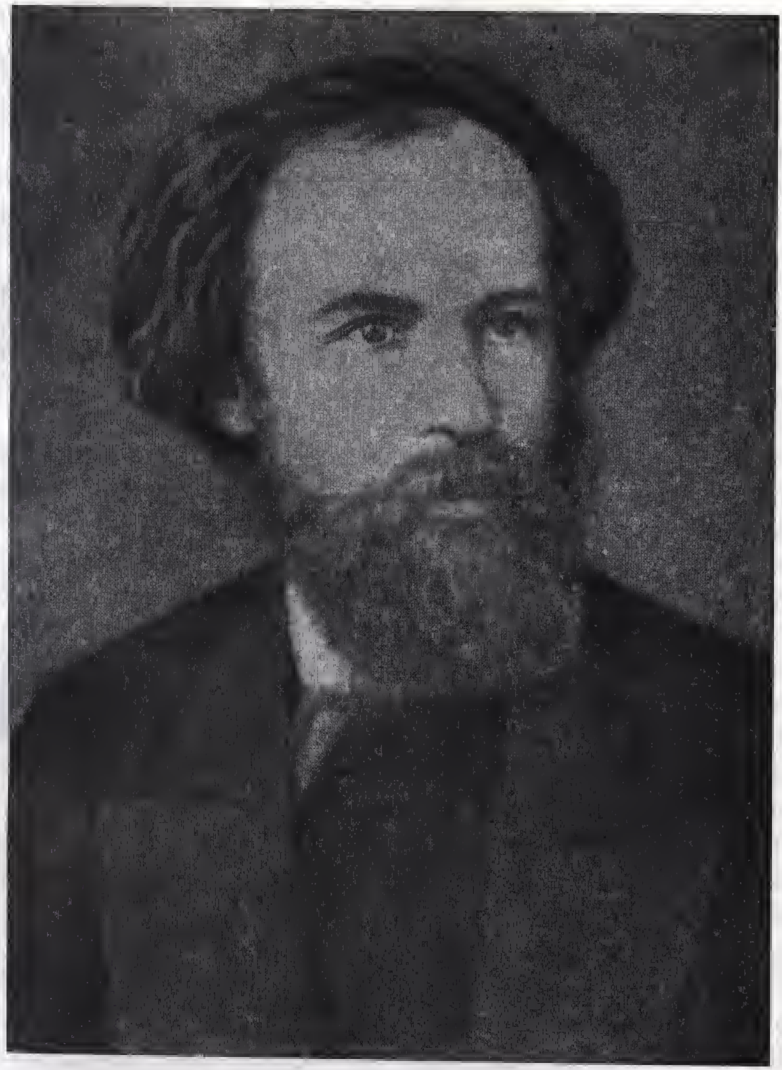
profess. de l'Univers. à S-Pétersbourg.

| | | | | | |
|---|---|---|---|---|---|
| | | | Ti=50 | Zr=90 | ?=180 |
| | | | V=51 | Nb=94 | Ta=182 |
| | | | Cr=52 | Mo=96 | W=186 |
| | | | Mn=55 | Rh=104,4 | Pt=197,4 |
| | | | Fe=56 | Ru=104,4 | Ir=198 |
| | | | Ni=Co=59 | Pl=106,6 | Os=199 |
| H=1 | | | Cu=63,4 | Ag=108 | Hg=200 |
| | Be=9,4 | Mg=24 | Zn=65,2 | Cd=112 | |
| | B=11 | Al=27,4 | ?=68 | Ur=116 | Au=197? |
| | C=12 | Si=28 | ?=70 | Sn=118 | |
| | N=14 | P=31 | As=75 | Sb=122 | Bi=210? |
| | O=16 | S=32 | Se=79,4 | Te=128? | |
| | F=19 | Cl=35,5 | Br=80 | I=127 | |
| Li=7 | Na=23 | K=39 | Rb=85,4 | Cs=133 | Tl=204. |
| | | Ca=40 | Sr=87,6 | Ba=137 | Pb=207. |
| | | ?=45 | Ce=92 | | |
| | | ?Er=56 | La=94 | | |
| | | ?Yt=60 | Di=95 | | |
| | | ?In=75,6 | Th=118? | | |

18 $\frac{III}{I}$ 69

Fig. 1.
Premier tableau de la classification périodique des éléments de D. I. Mendéléev (1869).

d'Odling (1864) et de Lothar Meyer (1864), les octaves de Newlands (1866). Toutefois ces travaux étaient consacrés soit à des questions particulières de similitude entre des groupes d'éléments, soit à des re-



D. I. Mendéléev, 1869.

cherches de relations entre leurs poids atomiques. Aucun des auteurs cités n'a cherché de relations générales entre les propriétés de *tous* les éléments connus, personne avant Mendéléev n'a formulé la loi périodique.

Bien que Mendéléev eût maintes fois souligné que « c'est la valeur du poids atomique qui déterminait le caractère des éléments chimiques », il ne pensait pas que les facteurs essentiels, caractéristiques des éléments se bornaient uniquement aux poids atomiques. Les propriétés chimiques des composés qu'ils formaient avaient une importance tout aussi considérable pour définir la place des éléments dans la classification périodique. Dans plusieurs cas Mendéléev a classé les éléments sans les disposer par ordre des poids atomiques croissants. Tel fut le cas du cobalt et du nickel, du tellure et de l'iode.

La portée éminente scientifique et philosophique de sa découverte tenait en premier lieu de ce qu'il a établi une relation entre tous les éléments, entre leurs propriétés physiques et chimiques. Les groupes et les séries du système périodique sont devenus une assise ferme pour la mise en évidence les familles d'éléments apparentés.

La loi périodique a trouvé sa première application dans la correction des valences et des poids atomiques de plusieurs éléments dont les valeurs adoptées à l'époque étaient entachées d'erreurs. Cela concernait en particulier l'indium, le cérium et autres éléments de terres rares, le thorium et l'uranium. L'indium était considéré comme un élément bivalent et, d'après son poids atomique [1] (75,6) était disposé entre l'arsenic et le sélénium, bien que ses propriétés fussent manifestement différentes. Les mesures de la chaleur spécifique de l'indium métallique et l'examen détaillé des propriétés de ses combinaisons ont amené Mendéléev à conclure qu'il fallait considérer l'indium comme trivalent à son état d'oxydation supérieur. Dans ce cas son poids atomique devenait égal à 113 et cet élément devait prendre sa place dans le groupe III du système périodique entre le cadmium (Cd = 112) et l'étain (Sn = 118) en parfaite conformité avec ses propriétés chimiques. Toutefois, cette case du système périodique avait été occupée jusque là par l'uranium que l'on considérait comme un élément trivalent de poids atomique 116. Bientôt après Mendéléev conclut que l'uranium par ses caractéristiques chimiques était plus proche du molybdène et du tungstène que d'aluminium. Aussi, après avoir doublé la valeur de son poids atomique, l'a-t-il placé dans le groupe VI de sa classification.

Mendéléev avança des considérations analogues pour justifier la valence III des éléments apparentés au cérium (lanthane, etc.) que de nombreux chimistes considéraient à l'époque comme bivalents. Il a attribué la formule $CeO_2$ à l'oxyde supérieur du cérium et la formule $ThO_2$ (au lieu de ThO) à l'oxyde supérieur du thorium.

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(1) Ici et dans la suite nous indiquons les poids atomiques connus à l'époque.

En conformité avec cela furent calculés les nouvelles caleurs des poids atomiques pour les éléments indiqués.

On conçoit que le travail qui vient d'être décrit était loin d'être facile. Il suffit de penser qu'à l'époque de Mendéléev on ne disposait pas de méthodes de mesure directe des poids atomiques. Seule la règle de Dulong et Petit pouvait être de quelque secours dans ce domaine. K. Rammelsberg, chercheur très versé dans la chimie des terres rares, était opposé aux changements des poids atomiques du cérium, du didyme et du lanthane proposées par Mendéléev, quant à Lothar Meyer il opinait « qu'il était prématuré de changer les poids atomiques adoptés jusqu'alors en choisissant un point de départ aussi incertain », ayant en vue la loi périodique.

L'opinion de Mendéléev sur la nécessité de corriger les poids atomiques des métaux du groupe de platine de façon qu'ils aillent en croissant et non en diminuant dans la suite Os - Ir - Pt (comme cela découlait des données analytiques anciennes) a trouvé peu après sa confirmation. Pourtant l'hypothèse de Mendéléev que le poids atomique du tellure devait être inférieur à celui de l'iode ne s'est pas justifiée, et, nous le savons à présent, la cause en est liée au caractère des isotopes de ces deux éléments et non aux propriétés chimiques de leurs atomes. Malgré la contradiction apparente avec la règle fondamentale qui présidait à l'organisation du système périodique, savoir la distribution des éléments par ordre des poids atomiques croissants, Mendéléev laissa le tellure dans le groupe VI et l'iode dans le groupe VII, compte tenu de leurs valences et de leurs propriétés chimiques.

Ainsi, au bout de recherches très poussées, surmontant d'immenses difficultés Mendéléev réussit à bref délai (deux ans à peine) de mettre sur pied l'essentiel de son système périodique des éléments que nous continuons à utiliser jusqu'à nos jours (fig. 2).

Et pourtant dès le début Mendéléev put mettre en évidence des cases vides de son tableau. Dès sa première publication sur la loi périodique il émit l'hypothèse sur l'existence d'un grand nombre de corps simples, encore inconnus, dont quelques'uns devaient être, par exemple, analogues à l'aluminium et au silicium et avoir un poids atomique compris entre 65 et 75. Mendéléev était convaincu que la meilleure preuve étayant sa loi périodique serait la réalisation des prédictions qui en découlent. Aussi, deux ans après avoir découvert la périodicité, publia-t-il son article [3] annonçant en détail les propriétés physiques et chimiques de plusieurs éléments qui n'avaient pas encore été découverts. « J'ose le faire dans le seul but d'avoir la possibilité, ne fût-ce qu'à l'avenir, de me convaincre définitivement et de persuader d'autres chimistes de la justesse des hypothèses qui reposent à la base de mon système, lorsque l'un de ces corps

annoncés par moi aura été découvert ». Mendéléev a étudié le plus en détail les propriétés attendues des analogues inconnus du bore, de l'aluminium et du silicium qu'il a nommés provisoirement ekabore, ekaaluminium et ekasilicium (²).

Les éléments prédits par Mendéléev ont été découverts sous peu. En 1875 P. Lecoq de Boisbaudran, chimiste français, a trouvé dans la blende de zinc pyrénéenne un nouvel élément, le gallium, dont les propriétés coïncidaient avec celles que Mendéléev a prédites pour l'ekaaluminium. En 1879, au cours de ses études sur les terres d'ytterbium, le

| Ряды | Группа I — $R^2O$ | Группа II — RO | Группа III — $R^2O^3$ | Группа IV $RO^4$ $RO^2$ | Группа V $RH^3$ $R^2O^5$ | Группа VI $RH^2$ $RO^3$ | Группа VII RH $R^2O^7$ | Группа VIII — $RO^4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H=1 | | | | | | | |
| 2 | Li=7 | Be=9,4 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Na=23 | Mg=24 | Al=27,3 | Si=28 | P=31 | S=32 | Cl=35,5 | |
| 4 | K=39 | Ca=40 | —=44 | Ti=48 | V=51 | Cr=52 | Mn=55 | Fe=56, Co=59, Ni=59; Cu=63 |
| 5 | (Cu=63) | Zn=65 | —=68 | —=72 | As=75 | Se=78 | Br=80 | |
| 6 | Rb=85 | Sr=87 | ?Yt=88 | Zr=90 | Nb=94 | Mo=97 | —=100 | Ru=107, Rh=104, Pd=106, Ag=108 |
| 7 | (Ag=108) | Cd=112 | In=113 | Sn=118 | Sb=122 | Te=125 | J=127 | |
| 8 | Cs=133 | Ba=137 | ?Di=138 | ?Ce=140 | — | — | — | — — — — |
| 9 | (—) | — | — | — | — | — | — | |
| 10 | — | — | ?Er=178 | ?La=180 | Ta=182 | W=184 | — | Os=195, Ir=197, Pt=198, Au=199 |
| 11 | (Au=199) | Hg=200 | Tl=204 | Pb=207 | Bi=208 | — | — | |
| 12 | — | — | — | Th=231 | — | U=240 | — | — — — — |

Fig. 2.

Système périodique des éléments de D. I. Mendéléev (1871).

chimiste suédois L. Nilson a isolé des minéraux scandinaves — la gadolinite et l'euxénite une terre rare nouvelle qu'il a baptisé de scandium. Se dernier a été identifié avec l'ekabore. En 1886 analysant l'argyrodite le chimiste allemand C. Winkler a découvert le germanium, un nouvel élément dont les propriétés se sont trouvées être très proches de celles que Mendéléev avait prédites pour l'ekasilicium (table 1). Winkler a noté: « Il est peu probable qu'on puisse trouver une démonstration plus étonnante de la justesse de la théorie de périodicité que l'identification de l'ekasilicium hypothétique à cet élément nouvellement trouvé. Ce

(²) Eka - un (en Sanskrit): ici dans le sens de premier analogue, le plus proche.

n'est pas une simple confirmation d'une théorie hardie: c'est une extension manifeste des horizons de la chimie, un grand pas en avant dans le domain du savoir ».

TABLE I.

*Propriétés annoncées et propriétés expérimentalement trouvées du germanium.*

| Proprieté | Annoncé pour l'ekasilicium (Es*) | Trouvé pour le germanium |
|---|---|---|
| *Poids atomique* | Es 72 | Ge 72,60 |
| *Valence* | « Quatre (mais on pourra manifester une valence inférieure) » | 4 et 2 |
| *Elément libre* | | |
| Volume atomique | 13 environs | 13,5 |
| Poids spécifique | 5,5 environs | 5,36 |
| Fusibilité et volatilité | « Métal fusible capable de se volatiliser sous l'effet d'une forte chaleur ». | F = 958,5° Eb = 2700° |
| *Oxyde supérieur* | $EsO_2$ | $GeO_2$ |
| Volume moléculaire | 22 environ | 22,2 |
| Propriétés chimiques | « Propriétés acides, très faiblement basiques ». | Amphotère avec prédominance de propriétés acides |
| *Chlorure supérieur* | $EsCl_4$ | $GeCl_4$ |
| P. eb, °C | Voisin de 90° | 83,1° |
| Poids spécifique | 1,9 environ | 1,874 |
| Proprietés chimiques | « Est décomposé par l'eau » | Est facilement hydrolysé par l'eau |
| *Composés hydrogénés* | « On peut aussi s'attendre beaucoup à l'existence d'un composé hydrogéné » | On a obtenu $GeH_4$ et d'autres hydrures de germanium |
| | « $EsH_4$ doit se décomposer facilement en hydrogène et métal » | $GeH_4$ se décompose à 350° |
| *Composés organomitalliques* | « Il formera certainement des composés organométalliques » | On a obtenu beaucoup de composés organogermaniens |
| $R(C_2M_5)_4$: | | |
| P. eb, °C | 160° | 163,5° |
| Poids spécifique | 0,96 | 0,99 |

(*) Symbole utilisé par Mendéléev.

Mendéléev a décrit plus sommairement les propriétésat tendues des analogues di manganèse, tellure, césium, baryum, lanthane et tantale qui n'avaient pas encore été découverts. Une partie de ces éléments

devaient être découverts du vivant de Mendéléev, c'étaient le radium, l'actinium et le polonium. Les autres ont été isolés au cours du XX$^{me}$ siècle — ce furent le technétium, le rhénium, le francium et le protactinium.

Le système périodique eut à subir à la fin du XIX$^{me}$ siècle une sérieuse épreuve dont elle est sortie victorieusement. Après que Rayleigh et Ramsay (1894) eurent découvert l'argon dans l'atmosphère il semblait que cet élément ne trouve pas de place dans le système périodique. Cependant la découverte par Ramsay de l'hélium dans le gaz isolé de la clévéite a démontré qu'il existait un groupe d'éléments semblables à l'argon.

En 1897 Ramsay fit une conférence intitulée « Un gaz non encore découvert ». Comme il devait l'indiquer plus tard lui-même, dans cette conférence « à l'exemple de notre maître Mendéléev j'ai décrit, autant que c'était possible, les propriétés attendues et le comportement prédit d'un élément gazeux qui devait venir combler la lacune entre l'hélium et l'argon ». Bientôt après Ramsay a réussit d'isoler ce gaz de poids atomique 20 à partir de l'air liquide. Il lui a donné le nom de néon. Presque simultanément on avait découvert les analogues lourds de l'argon — le crypton et le xénon. Tous ces éléments selon les recherches de l'époque étaient caracterisés par leur inertie, leur inaptitude à entrer dans les réactions chimiques ordinaires d'oxydoréduction. La famille des gaz rares a trouvé une place pour cette raison dans le système périodique, sous la forme d'un groupe zéro nouvellement formé. En 1900 on a rattaché à ce groupe un élément radioactif — le radon (émanation du radium).

La découverte des éléments annoncés par Mendéléev, la coïncidence exacte des propriétées trouvées avec les valeurs précalculées en partant de la loi périodique, la confirmation des corrections apportées par Mendéléev aux poids atomiques, tout cela contribua à consolider les notions matérialistes sur les éléments chimiques et ouvrit des perspectives immenses à la connaissance de la Nature par l'Homme. Le système périodique devint une arme puissante pour les chercheurs en chimie et en physique.

En partant de la loi périodique on a entrepris la comparaison de diverses propriétés des éléments et de leurs combinaisons. Mendéléev avait démontré en 1869 la périodicité des formes de combinaisons constituées par les éléments c'est-à-dire de la caractéristique chimique essentielle qu'est la valence. C'est lui qui avait établi la périodicité des variations des poids spécifiques des corps simples et des volumes atomiques des éléments. D'autres chercheurs ont démontré que les points de fusion des corps simples varient périodiquement. On a constaté qu' il en était de même des points de fusion des chlorures de métaux. On avait observé la périodicité dans la quantité de chaleur dégagée au cours de la formation des chlorures, bromures et iodures au fur et à mesure de l'accroissement des poids atomiques des éléments qui réagissent avec les halogènes.

## Періодическая система элементовъ по группамъ и рядамъ.

| Ряды. | ГРУППЫ ЭЛЕМЕНТОВЪ: 0 | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|---|
| 1 | — | Водородъ. H 1,008 | — | — | — | — | — | — | |
| 2 | Гелій. He 4,0 | Литій. Li 7,03 | Берилій. Be 9,1 | Боръ. B 11,0 | Углеродъ. C 12,0 | Азотъ. N 14,01 | Кислородъ. O 16,00 | Фторъ. F 19,0 | |
| 3 | Неонъ. Ne 19,9 | Натрій. Na 23,05 | Магній. Mg 24,36 | Алюминій. Al 27,1 | Кремній. Si 28,2 | Фосфоръ. P 31,0 | Сѣра S 32,06 | Хлоръ Cl 35,45 | |
| 4 | Аргонъ. Ar 38 | Калій. K 39,15 | Кальцій. Ca 40,1 | Скандій. Sc 44,1 | Титанъ. Ti 48,1 | Ванадій. V 51,2 | Хромъ. Cr 52,1 | Марганецъ. Mn 55,0 | Желѣзо. Fe 55,9 Кобальтъ. Co 59 Никкель. Ni 59 (Cu) |
| 5 | | Мѣдь Cu 63,6 | Цинкъ. Zn 65,4 | Галлій. Ga 70,0 | Германій. Ge 72,5 | Мышьякъ. As 75 | Селенъ. Se 79,2 | Бромъ. Br 79,95 | |
| 6 | Криптонъ. Kr 81,8 | Рубидій. Rb 85,5 | Стронцій. Sr 87,6 | Иттрій. Y 89,0 | Цирконій. Zr 90,6 | Ніобій. Nb 94,0 | Молибденъ. Mo 96,0 | — | Рутеній. Ru 101,7 Родій Rh 103,0 Палладій. Pd 106,5 (Ag) |
| 7 | | Серебро. Ag 107,93 | Кадмій. Cd 112,4 | Индій. Jn 115,0 | Олово. Sn 119,0 | Сурьма. Sb 120,2 | Теллуръ. Te 127 | Іодъ. J 127 | |
| 8 | Ксенонъ. Xe 128 | Цезій. Cs 132,9 | Барій. Ba 137,4 | Лантанъ. La 138,9 | Церій. Ce 140,2 | — | — | — | — — — |
| 9 | | — | — | — | — | — | — | — | |
| 10 | — | — | — | Иттербій. Yb 173 | — | Танталъ. Ta 183 | Вольфрамъ. W 184 | — | Осмій. Os 191 Иридій. Jr 193 Платина. Pt 194,8 (Au) |
| 11 | | Золото. Au 197,2 | Ртуть. Hg 200,0 | Талій. Tl 204,1 | Свинецъ. Pb 206,9 | Висмутъ. Bi 208,5 | — | — | |
| 12 | — | — | Радій. Rd 225 | — | Торій. Th 232,5 | — | Уранъ. U 238,5 | | |
| Высшіе солеобразные окислы: | R | $R^2O$ | $RO$ | $R^2O^3$ | $RO^2$ | $R^2O^5$ | $RO^3$ | $R^2O^7$ | $RO^4$ |
| Высшія газообразныя водородныя соединенія: | | | | | $RH^4$ | $RH^3$ | $RH^2$ | $RH$ | |

*Д. Менделѣевъ.*
1869 – 1905.

Fig. 3.
Système périodique des éléments de D. I. Mendéléev (1905).

Mendéléev a remarqué également (1889) la périodicité de la structure des spectres d'éléments en fonction des poids atomiques. On a découvert un rapport entre la position des éléments dans le système périodique et leurs propriétés magnétiques. En prenant comme exemple les alliages du cuivre A. A. Baïkov a démontré (1902) l'applicabilité des principes de la périodicité à la composition des combinaisons métalliques qui se forment dans les alliages.

Pendant de longues années qui ont suivi la découverte de la loi périodique Mendéléev continuait à perfectionner son tableau des éléments. Il l'utilisait d'ailleurs sous sa forme courte ou sous sa forme longue. La fig. 3 représente le dernier tableau dressé par Mendéléev peu avant sa mort, en 1907.

La loi périodique et le système des éléments qui en dérive ont remporté d'immenses succès du vivant de Mendéléev. Toutefois quelques parties de ce système restaient encore à préciser. On ne savait pas notamment s'il devait y exister des éléments entre l'hydrogène et l'hélium, le nombre des terres rares restait imprécis, de même que leur position dans le système périodique. Toutes ces difficultés ne permettaient pas de calculer le nombre totale d'éléments entre l'hydrogène et l'uranium. La cause même de la périodicité restait obscure. Il faut s'émerveiller du génie de Mendéléev qui avait réussi à créer son système périodique des éléments dans l'absence presque totale de renseignements sur la constitution de la matière et qui est parvenu à l'édifier de façon que, cent ans après, ce tableau ne demande aucune modification sérieuse.

Après la mort de Mendéléev, la loi périodique a exercé une influence énorme sur les travaux des physiciens et des chimistes dans le domaine de la constitution de la matière.

***

Tout d'abord il faut souligner le rôle du système périodique dans l'explication des phénomènes de la radioactivité et dans la découverte des isotopes. La mise en évidence par Becquerel (1896) des « rayons de l'uranium » avec leurs propriétés extraordinaires, suscita une multitude de travaux consacrés à cette nouvelle branche de la science. Outre l'uranium, on a trouvé que le thorium, dutre élément lourd, manifestait la radioactivité. En 1898 Marie et Pierre Curie découvrirent dans les minerais uranifères deux éléments nouveaux: le radium et le polonium qui manifestaient une radioactivité encore plus intense que l'uranium. Une préparation de radium à l'état pur a été isolée par eux à partir des dechets du traitement de mineral uranifère. Cet élément s'est révélé analogue

au barium et correspondait par ses propriétés chimiques à l'ekabarium de Mendéléev. Les propriétés du polonium étaient très voisines de celles de l'ekatellure.

En 1899 Debierne trouva dans la pechblende uranifère un autre élément radioactif, l'actinium, analogue du lanthane. L'existence de cet élément avait été prédite par Mendéléev dès 1871.

En 1900 il a été établi que les préparations du radium dégageaient d'une manière permanente un gaz radioactif, l'émanation du radium, que l'on a identifié comme un analogue du xénon appartenant au groupe zéro du système périodique et que l'on appelle aujourd'hui le radon. Une propriété remarquable du radon est sa désintégration rapide, sa période étant de 3,85 jours. Ramsay et Soddy en 1902 ont trouvé que l'émanation du radium scellée dans un tube à décharge commençait à manifester au bout d'un certain temps le spectre de l'hélium. Ce fut le premier cas, scientifiquement établi de transmutation des éléments.

Mendéléev émettait des doutes sérieux sur la possibilité de la transmutation des éléments. Il estimait que toutes les communications à ce sujet demandaient à être consciencieusement vérifiées et que géneralement elles ne se confirmaient pas. Toutefois il se considérait « non pas comme un adversaire, mais plutôt comme enclin à adopter la notion de la complexité des éléments ». Il écrivait (1898) qu'il « serait fort intéressant d'assister à l'établissement de données prouvant les transmutations mutuelles des éléments, car je pourrais alors espérer que la cause de la loi périodique serait élucidée et comprise ». Nous voyons que quelques années plus tard les progrès de la science ont donné une valeur d'actualité à ce problème.

En 1902 Rutherford et Soddy qui ont effectué une étude détaillée de la radioactivité du thorium ont suggéré que les phénomènes de la radioactivité étaient liés à des atomes et, par conséquent, des éléments. Les recherches ultérieures ont démontré le bien-fondé de cette hypothèse.

Les études sur l'émanation du radium ont indiqué que le « résidu radioactif » de sa désintégration contenait plusieurs éléments qui différaient entre eux par leurs propriétés radioactives c'est-à-dire par le caractère et l'énergie du rayonnement. Beaucoup d'éléments radioactifs ont été découverts au cours des études sur les transmutations de l'uranium, de l'actinium et du thorium.

Seule une partie des éléments radioactifs nouvellement découverts a pu être distribuée entre les cases vides du système périodique. Les recherches sur un grand nombre d'éléments radioactifs qui appartenaient aux différentes familles radioactives, ont permis d'établir que nombre d'entre

eux, tout en différant par leurs propriétés radioactives, ne peuvent être séparés par des moyens chimiques les uns des autres ou de certains éléments ordinaires. C'est ainsi que l'un des produits de la désintegration de l'uranium, l'élément radioactif nommé ionium tout en différant nettement par sa radioactivité du thorium, ne peut en être séparé par un procédé chimique. L'un des premiers produits de la décomposition du thorium, le radio-thorium, qui se désintègre beaucoup plus vite que le thorium, est absolument identique à ce dernier au point de vue chimique. Ainsi il s'est trouvé qu'un grand nombre d'éléments radioactifs nouvellement découverts, ne différaient pas par leurs propriétés chimiques de l'uranium, du thorium, radium, plomb, bismuth et autres éléments des deux lignes (séries) horizontales inférieures du système périodique. On arrivait à cette conclusion qu'à un même élément chimique correspondaient plusieurs séries d'atomes qui differaient par leur masse et par la vitesse de leur désintégration radioactive.

En 1913 Soddy a proposé d'appeler « isotopes » ces variétés d'éléments, marquant ce fait caractéristique qu'ils occupaient une même place dans le système périodique (isos-identique, topos-place).

Les nombreux éléments radioactifs qui se forment par désintégration de l'uranium, du thorium ou de l'actinium ont été désormais réunis en familles harmonieusement liées au système périodique de Mendéléev. Tout acte de radiation alpha donnait un produit qui était un isotope de l'élément rétrogradé de deux places dans le système périodique. La désintégration, bêta amenait à un élément qui était d'une case déplacé vers la fin du système. Cette règle, dite de déplacement, établie par Fajans et Soddy, a permis de découvrir un grand nombre d'éléments radioactifs nouveaux et mettre en ordre certaine points obscurs des familles radioactives.

En 1913 J. J. Thomson appliqua le procédé d'analyse électromagnétique à des faisceaux de rayons canaux, obtint les premiers renseignements sur l'existence des isotopes d'éléments non radioactifs dans le cas du néon. La création du spectrographe des masses par Aston permit de détecter des isotopes de plusieurs éléments ordinaires.

Le phénomène d'isotopie a injecté un sang nouveau dans le système périodique. On eut désormais une brillante confirmation des hypothèses formulées par Boutlérov, Crookes et d'autres savants sur la possibilité d'existence de variétés d'atomes d'un même élément qui diffèrent légèrement par leur masse. D'autre part la découverte (beaucoup plus récente) d'une différence notable entre les propriétés chimiques des isotopes de l'hydrogène a ouvert en chimie un chapitre nouveau, celui de la chimie des isotopes, étroitement lié au système périodique.

***

On sait que la découverte de la radioactivité et les progrès impétueux de la physique atomique au début du XX^me^ siècle firent naître la théorie nucléaire de la constitution atomique (Rutherford, 1911), entraînèrent la découverte de la loi reliant la longueur d'onde des spectres caractéristiques des rayons X d'éléments aux charges de leurs noyaux nucléaires (Moseley, 1913) et la création de la théorie de structure atomique à base de la théorie des quanta (Bohr, 1913). La loi périodique exerça une influence très marquée sur la recherche orientée dans ces voies car elle mit à la disposition des savants un système naturel d'éléments chimiques avec toutes les lois latents de la constitution des atomes qu'il impliquait.

D'autre part, la théorie moderne de la constitution atomique permit d'élucider les causes intimes de la périodicité même et de mieux prévoir les propriétés des éléments encore inconnus. C'est le procédé de la détermination expérimentale des charges nucléaires fondé sur la loi de Moseley qui joua un rôle capital. Ce procédé permit de définir exactement les numéros d'ordre des éléments dans le système périodique et d'établir le nombre totale de ces éléments compris entre l'hydrogène et l'uranium. On put confirmer la distribution de tous les éléments dans le tableau de Mendéléev. On a trouvé que le numéro atomique de l'iode (53 était supérieur à celui du tellure (52). En 1914 seules les cases n. 43, 61, 72, 75, 85, 87 et 91 restaient vides. Parmi celles-ci les n. 61, 72, 75 et 85 se rapportaient à la III^me^ grande période.

La théorie de la constitution des atomes a permis d'expliquer les particularités de la position des éléments de terres rares dans le système périodique qui suivent le lanthane dans la III^me^ grande période. Il s'est trouvé que dans cette partie du système les électrons des atomes d'éléments à partir du cérium, entrent dans la couche profonde du quatrième niveau pour venir se placer sur le sous-niveau 4f qui peut comporter jusqu'à 14 électrons et dont le complètement s'achève avec le lutécium. Le nombre d'électrons de valence ne varie pas et reste, comme pour le lanthane, égal à trois. Pour cette raison à l'heure actuelle on réunit généralement les éléments de la famille Ce - Lu sous le nome générique de lanthanides. On les classe dans la même case que le lanthane et on les dénombre dans une série séparée au bas du tableau.

La structure des couches électroniques des atomes de terres rares, d'après les données actuellement disponibles, est indiquée schématiquement dans la table II.

TABLE II.

*Structure des couches électroniques des atomes des elements de terres rares.*

| Elément | Numéro atomique Z | Niveaux d'énergie des atomes | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n = 1 | n = 2 | n = 3 | | n = 4 | | | | n = 5 | | | n = 6 |
| | | K | L | M | | N | | | | O | | | P |
| | | s | s, p | s, p | d | s | p | d | f | s | p | d | s |
| Sc | 21 | 2 | 8 | 8 | 1 | 2 | | | | | | | |
| Y | 39 | 2 | 8 | 8 | 10 | 2 | 6 | 1 | | 2 | | | |
| La | 57 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | | 2 | 6 | 1 | 2 |
| Ce | 58 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 2 | 2 | 6 | | 2 |
| Pr | 59 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 3 | 2 | 6 | | 2 |
| Nd | 60 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 4 | 2 | 6 | | 2 |
| Pm | 61 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 5 | 2 | 6 | | 2 |
| Sm | 62 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 6 | 2 | 6 | | 2 |
| Eu | 63 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 7 | 2 | 6 | | 2 |
| Gd | 64 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 7 | 2 | 6 | 1 | 2 |
| Tb | 65 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 9 | 2 | 6 | | 2 |
| Dy | 66 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 10 | 2 | 6 | | 2 |
| Ho | 67 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 11 | 2 | 6 | | 2 |
| Er | 68 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 12 | 2 | 6 | | 2 |
| Tu | 69 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 13 | 2 | 6 | | 2 |
| Yb | 70 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 14 | 2 | 6 | | 2 |
| Lu | 71 | 2 | 8 | 8 | 10 | 2 | 6 | 10 | 14 | 2 | 6 | 1 | 2 |

Note: n - nombre quantique principal; K, L, M, ... - niveaux d'énergie des atomes; s, p, d, f - groupes d'électrons.

Ainsi qu'il découle du tableau, deux électrons de valence des lanthanides se rapportent au sous-niveau Cs, alors que le troisième se détache généralement du sous-niveau 4f et ne se trouve au sous-niveau 5d que chez un petit nombre de termes de cette série. Au début de la formation de la couche électronique 4f, les électrons qui la forment, ne sont pas liés très fermement. Aussi le cérium, le praséodyme et probablement le néodyme sont-ils capables de constituer des combinaisons dans lesquels leur valence est égale à 4. Ensuite la charge croissante du noyau consolide la structure de l'enveloppe considérée. Il convient d'ajouter qu'elle se complète probablement en deux couches dont chacune se compose de sept électrons. Pour cette raison le terbium manifeste, lui aussi, l'aptitude à la formation de composés correspondants à la valence supérieure, cet élément étant caractérisé par le remplissage de la secone couche. Les éléments qui précèdent le gadolinium (c.à.d. le samarium et l'euro-

pium) et le lutécium (c.à.d. l'ytterbium) peuvent, au contraire, se rapprocher par leur structure d'une configuration plus stable en cédant un nombre inférieur d'électrons. Aussi sont-ils bivalents dans certains cas.

Des recherches ultérieures ont permis d'établir une loi importante sur la variation des dimensions d'atomes des lanthanides [4]. Les électrons appartenant à la couche profonde 4f n'arrivent pas à protéger complètement la charge croissante du noyau. Aussi les électrons des couches extérieures sont-ils attirés par le noyau, et les dimensions globales de l'atome sont-elles réduites (c'est la contraction lanthanidique).

Nous indiquons dans ce qui suit les valeurs des rayons ioniques des terres rares à l'état trivalent.

Rayon ionique, Å

| Sc | Y | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd |
|---|---|---|---|---|---|---|---|---|---|
| 0,68 | 0,88 | 1,04 | 1,02 | 1,00 | 0,99 | (0,98) | 0,97 | 0,96 | 0,94 |

| Tb | Dy | Ho | Er | Tu | Yb | Lu |
|---|---|---|---|---|---|---|
| 0,92 | 0,91 | 0,89 | 0,87 | 0,86 | 0,85 | 0,84 |

La contraction lanthanidique amène l'affaiblissement des propriétés basiques des hydroxydes dans la suite La—Lu. Si$La(OH)_3$ est proche par ses propriétés de Sr/$(OH)_2$, $Lu(OH)_3$, par contre, est une base faible et s'apparente à ce point de vue, à l'hydroxyde de scandium, élément disposé beaucoup plus haut dans le même groupe du système périodique. Le dysprosium et l'holmium sont proches, du point de vue considéré, de l'yttrium.

Ainsi les similitudes de structure de la couche électronique des atomes et la contraction lanthanidique ont transformé le scandium, l'yttrium, le lanthane et les lanthanides en un ensemble d'éléments étroitement embrouillés proches les uns des autres par leurs propriétés et des conditions de leur présence dans les minerais. Cela, à son tour explique toutes les difficultés qui s'opposent à leur séparation, leur purification et à leur identification.

La théorie de la constitution des atomes a montré que l'élément n. 72 qui vient après le lutécium, devait avoir deux électrons de valence à chacun des sous-niveaux 6s et Sd. Aussi devait-il être tétravalent et présenter des analogies avec le zirconium, et non avec les terres rares. En partant de là les recherches de l'élément n. 72 entreprises par Hevesy et Coster au moyen de spectres des rayons X dans les préparations de zirconium ont été couronnées de succès et cet élément a été effectivement découvert en 1923. Il a reçu le nom d'hafnium (Hf = 178,5). Notons que

l'analogue du zirconium de poids atomique 180 avait été prédit par Mendéléev dès la première version de sa classification (voir plus haut).

Ainsi est-on arrivé à défaire le noeud des terres rares dans le système périodique. Les éléments manquants de ce système au moment de la découverte de la loi de Moseley ont pu être isolés à un assez bref délai à partir des matières naturelles, ou bien ont été préparés par synthèse nucléaire.

En 1918 Meitner et Hahn ont isolé à partir des résidus de préparation des minerais uranifères l'élément radioactif n. 91 - le protactinium. En 1925 Noddack, Takke et Berg ont découvert dans le platine cru, dans des échantillons de tantalite et de molybdénite l'élément n. 75 qu'ils ont nommé le rhénium. La mise en évidence par ces mêmes auteurs de l'élément n. 43 n'a pas été confirmée par la suite. Il n'a été découvert qu'en 1937 par Perrier et Segré dans un échantillon de molybdène soumis à une irradiation prolongée par un flux intense de deutons dans un cyclotron. La réaction nucléaire se déroulait schématiquement comme suit $_{42}Mo(d, n)43$. Après identification, cet élément a reçu le nom de technétium qui devait traduire son mode de préparation artificiel.

Il a été établi plus tard que le technétium était présent en quantités considérables dans les produits de fissions de l'uranium et pouvait être extrait des résidus de l'industrie nucléaire.

En étudiant les produits de la désintégration radioactive naturelle de l'actinium Pérey y a découvert un isotope radioactif (période 21 mn), analogue par son comportement chimique au césium. Cet élément a été identifié comme le n. 87 - ekacésium prédit par Mendéléev. Il a reçu le nom de francium.

L'isotope radioactif d'ekaiode — élément n. 85 (période 7,5 h) a été découvert en 1940 par Corson, Mackenzie et Segré dans lex produits de bombardement du bismuth par les noyaux accelerés d'hélium avec l'énergie de 38 MeV. Le phénomène se déroulait schématiquement comme suit: $_{83}Bi^{209}(_2He^4, 2n)85^{211}$.

Le nom d'astate qu'a reçu cet élément son instabilité.

Enfin l'élément n. 61 qui a été recherché pendant longtemps sans succès par de nombreux chimistes dans les préparations de terres rares a été découvert finalement en 1947 parmi les produits de fission de l'uranium. Il a été identifié par Marinski, Glendenin et Coryell sous forme de deux isotopes radioactifs, de 55 h et de 2,6 années de période. Cet élément a reçu le nom de prométhium pour commémorer la découverte des applications pratiques de l'énergie atomique que ces chimistes comparaient au feu du ciel ravi par Prométhée.

Ainsi vers 1947 toutes les cases du système périodique entre l'hydrogène et l'uranium avaient été remplies.

Des problèmes entièrement nouveaux ont été posés (en ce qui concerne le système périodique) par les progrès de la synthèse de nouveaux éléments lourds [5]. Notons à ce propos que Mendéléev avait prévu l'extension de la classification périodique au-delà de l'uranium, et cette hypothèse a été confirmée.

L'idée de la synthèse des éléments transuraniens devint à l'ordre du jour au cours des annés trente lorsque Fermi et ses collaborateurs ont mis sur pied un procédé de préparation artificielle des isotopes radioactifs au moyen de neutrons lents. En 1935 ils ont découvert dans l'uranium irradié par des neutrons plusieurs isotopes radioactifs de brève vie, émettant des rayons bêta, dont l'un (période: 13 mn) était coprécipité avec le manganèse et le rhénium et a été pris pour l'analogue du rhénium ${}_{93}\mathrm{Eka/Re}^{239}$. Pourtant les recherches ultérieures de L. Meitner, Hahn et Strassmann ont montré que dans ces expériences il se formait beaucoup d'isotopes radioactifs — fragments de la fission de l'uranium qui coprécipitaient avec des éléments variés. On a trouvé parmi eux un émetteur du rayonnement bêta (période: 23 mn) qui ne différait pas, par ses propriétés chimiques, de l'uranium et que l'on supposait être son isotope ${}_{92}\mathrm{U}^{293}$. Par désintégration bêta il devait se transformer en élément n. 93. Toutefois les auteurs n'ont pas réussi à y détecter le nouvel élément par suite de la faible intensité de la source de neutrons utilisée.

L'élément n. 93 appelé neptunium (Np) a été découvert par McMillan et Abelson en 1940 par irradiation de minces couches d'uranate d'ammonium avec un flux intense de neutrons. On obtient ces derniers en bombardant une plaque de beryllium par des deutons de 16 MeV dans le grand cyclotron de l'Université de Californie. Les fragments de fission de l'uranium étaient éliminés grâce au phénomène du recul. Dans la préparation d'uranium on a trouvé deux genres d'activité bêta (périodes 23 mn et 2,9 j). La nature de la première était comme: elle prevenait de ${}_{92}\mathrm{U}^{239}$. La transmutation du premier émetteur en second servit à prouver la formation de l'élément n. 93. McMillan et Abelson ont conclu que le neptunium n'était pas un élément analogue au rhénium. On a trouvé qu'il pouvait se présenter à au moins deux états d'oxydation. A son état d'oxytadion inférieur le neptunium est analogue aux terres rares. Dans les composés correspondant à l'état d'oxydation supérieur il est semblable à l'uranium.

Dans la désintégration bêta du neptunium il fallait s'attendre à la formation de l'élément n. 94. Ce corps a reçu le nom de plutonium (Pu). Son premier isotope $\mathrm{Pu}^{238}$ (période: 89,6 années) a été préparé fin 1940 par Seaborg, McMillan, Kennedy, Wahl. Procédé utilisé: bombardement de l'uranium par deutons au cyclotron. Comme intermédiaire on obtenait ${}_{93}\mathrm{Np}^{238}$ (période: 2,1 j):

$${}_{92}\mathrm{U}^{238} + {}_{1}\mathrm{H}^{2} = {}_{93}\mathrm{Np}^{238} + 2\mathrm{n}\,; \qquad {}_{93}\mathrm{Np}^{238} - {}_{94}\mathrm{Pu}^{238} + \bar{\beta}\,.$$

A l'échelle traceur on a réussi à étudier les propriétés du nouvel isotope et les principes de sa séparation de l'uranium. A l'étalt de valence supérieure le plutonium est analogue à l'uranium, mais se prête plus facilement à la réduction. Les propriétés des composés de plutonium correspondant à sa valence inférieure rappellent celles du thorium et des terres rares. Pour des raisons d'ordre militaire les premiers renseignements sur le plutonium n'ont été publiés qu'en 1946.

Notons qu'en 1941, après un bombardement prolongé de l'uranium par les deutons au cyclotron on a découvert un autre isotope de plutonium $Pu^{239}$ (période: 24360 années) fissile sous l'effet des neutrons lents. Pour cette raison ce corps acquit plus tard une importance pratique considérable comme l'un des types de combustible nucléaire.

Après des travaux laborieux comprenant l'irradiation de quelques dizaines de kilogrammes de nitrate d'uranyle par des neutrons au cyclotron, on a réussi à isoler vers la fin de 1942 0,5 mg de plutonium sous la forme de composés purs. Ces recherches ont été poursuivies sur la première pile de laboratoire à l'uranium dont la mise en service eut lieu le 2 décembre 1942 à l'Université de Chicago. Parallèlement on poursuivait les études d'une unité pilote destinée à isoler le plutonium à partir de l'uranium irradié dans une pile avec un facteur de conversion de $10^{10}$ jamais atteint jusque là dans l'industrie chimique. La première pile industrielle est entrée un an après en service.

Au bout d'un mois et demi on commença l'exploitation de la première unité expérimentale de séparation, et peu de temps après les chercheurs disposaient déjà de quelques grammes de cet élément. En septembre 1944 on a mis en service la première usine qui fournit des kilogrammes de plutonium. Ainsi une période de trois ans s'était à peine écoulée entre la première obtention artificielle du nouvel élément et son isolation à l'échelle industrielle! A l'heure actuelle le plutonium est produit dans quelques pays, et les quantités livrées annuellement se chiffrent par tonnes.

L'extension de nouvelles recherches sur les transuraniens est étroitement liée aux travaux de l'éminent savant américain Seaborg et de ses collaborateurs. Entre 1944 et 1955 on a découvert sept autres éléments transuraniens. L'américium (Am, n. 95) a été obtenu en irradiant le plutonium par des neutrons, le curium (Cm, n. 96), le berkelium (Bk, n. 97) et le californium (Cf, n. 98) — en bombardant par des ions d'hélium de hautes énergies des cibles contenant respectivement le plutonium, l'américium ou le curium. Les isotopes de l'einsteinium (Es, n. 99) et du fermium (Em, n. 100) ont été mis en évidence par irradiation de l'uranium avec un flux instantané très intense de neutrons qui a accompagné l'explosion thermonucléaire de 1952. Sous l'effet de la capture multiple de neu-

trons il s'est formé des isotopes très lourds d'uranium qui se sont ensuite désintégrés avec émission de particules bêta et formation de plusieurs éléments transuraniens, y compris de l'einsteinium et du fermium. Plus tard ces éléments ont été préparés par d'autres voies. On a obtenu l'élément n. 101 en agissant par des ions hélium de hautes énergies (41 MeV) sur l'einsteinium. Au cours des premières expériences on a identifié au total 17 atomes du nouvel élément par sa transmutation en fermium. Les auteurs ont donné à l'élément n. 101 le nom de mendélévium (Md) « pour marquer le rôle éminent du grand chimiste russe, Dmitri Mendéléev qui le premier utilisa le tableau périodique des éléments pour prédire les propriétés chimiques des éléments non encore découverts, — principe-clef pour la découverte des sept derniers éléments transuraniens (actinides)... ».

La table 3 résume les schémas des premières réactions nucléaires qui ont servi à préparer les éléments transuraniens ainsi que les noms des auteurs de ces découvertes.

En 1957 on annonça pour la première fois la découverte de l'élément n. 102. Un groupe de chercheurs, Fields, Milstead, Atterling etc. ont irradié une préparation de curium par des ions de carbone-13 suivant le schéma:

$$_{96}Cm^{244}(C^{13}, 6n)102^{251}$$

ou

$$_{96}Cm^{244}(C^{13}, 4n)\ 102^{253}\ .$$

Les produits de cette réaction nucléaire avaient une période d'environ 10 mn. On a proposé pour le nouvel élément le nom de nobélium. Toutefois ces résultats n'ont pas été confirmés par vérification au laboratoire de Seaborg.

La même année en U.R.S.S. Flerov, Polikanov, Karamian et alia ont observé en irradiant le plutonium-241 par un flux d'ions d'oxygène à 5 charges, des particules alpha de 8 à 9 MeV d'énergie qui pouvaient être attribuées à l'isotope $102^{253}$ dont la période est de quelques secondes à une minute. Son identification chimique n'a pas été effectuée.

En 1958-1959 Ghiorso, Seaborg et al. ont à maintes reprises essayé d'obtenir des isotopes de l'élément n. 102 suivant les schémas:

$$_{96}Cm^{246}(C^{12}, 4n)\ 102^{254}\ ; \qquad _{96}Cm^{244}\ (C^{13}, 4n)\ 102^{253}\ ,$$

mais n'ont détecté que des produits à période de l'ordre de quelques secondes. Les auteurs de la communication primaire sur l'élément n. 102 ont également modifié leur point de vue et pensèrent que leurs expé-

TABLE III.

*Histoire de la découverte des éléments transuraniens.*

| Elément | Nombre atomique | Année de la découverte | Schéma des réactions nucléaires | Auteurs de la decouverte |
|---|---|---|---|---|
| Np | 93 | 1940 | ${}_{92}U^{238}(n, \gamma)_{92}U^{239}$; ${}_{92}U^{239} = {}_{93}Np^{231} + \bar{\beta}$ | McMillan, Abelson |
| Pu | 94 | 1940 | ${}_{92}U^{236}({}_1H^2, 2n)_{93}Np^{236}$; ${}_{93}Np^{236} = {}_{94}Pu^{236} + \beta$ | Seaborg, McMillan, Kennedy, Wahl. |
| Am | 95 | 1944 | ${}_{94}Pu^{239} + 2n = {}_{94}Pu^{24-}$; ${}_{94}Pu^{241} = {}_{95}Am^{241} + \beta$ | Seaborg, James, Morgan, Ghiorso, |
| Cm | 96 | 1944 | ${}_{94}Pu^{239}({}_2He^4, n)_{96}Cm^{242}$ | Seaborg, James, Ghiorso. |
| Bk | 97 | 1949 | ${}_{95}Am^{241}({}_2He^4, 2n)_{97}Bk^{243}$ | Thompson, Ghiorso, Seaborg. |
| Cf | 98 | 1950 | ${}_{96}Cm^{242}({}_2He^4, n)_{96}Cf^{245}$ | Thompson, Street, Ghiorso, Seaborg. |
| Es | 99 | 1955 | ${}_{92}U^{236} + 15n = {}_{92}U^{253}$; ${}_{92}U^{253} \xrightarrow[6\beta]{} {}_{96}Cf^{253} \xrightarrow[\beta]{} {}_{99}Es^{253}$ | Ghiorso, Thomps., Higgins, Seaborg. |
| Fm | 100 | 1955 | ${}_{92}U^{236} + 17n = {}_{92}U^{255}$; ${}_{92}U^{255} \xrightarrow[x\beta]{} {}_{99}Es^{255} \xrightarrow[\beta]{} {}_{100}Fm^{255}$ | Les mêmes. |
| Md | 101 | 1955 | ${}_{99}Es^{253}({}_2He^4, n)_{101}Md^{256}$ | Ghiorso, Harvey, Choppin, Thomps., Seaborg. |
| No(?) | 102 | 1957 | ${}_{96}Cm^{244}(C^{13}, 4n)102^{253}$; ${}_{96}Cm^{246}(C^{12}, 4n)102^{254}$; ${}_{94}Pu^{241}({}_8O^{16}, 4n)102^{253}$; | Divers auteurs. |
| Lr | 103 | 1961 | ${}_{96}Cf^{252}(B^{11}, 6n)103^{257}$; ${}_{98}Cf^{250}(B^{10}, 3n)103^{257}$ | Ghiorso, Sikkeland, Larsh, Latimer. |
| Ku | 104 | 1966 | ${}_{94}Pu^{242}({}_{10}Ne^{22}, 4n)104^{260}$ | Flerov, Drouine, Zvara et al. |

riences avaient abouti à l'isotope $102^{255}$. En 1963 les chercheurs soviétiques Flerov, Donets, Chtchegolev et al. ont synthétisé l'isotope de l'élément n. 102 de nombre de masse 256. Ils ont utilisé à cet effet un puissant accélérateur d'ions à charges multiples. L'uranium métallique a été bombardé par des noyaux de néon de hautes énergies. On a trouvé que la période du nouvel isotope était voisine de 8 mn. Ainsi le problème de la synthèse de l'élément n. 102 a été sensiblement résolu, mais son nom n'est pas encore universellement adopté.

Au début de 1961 Ghiorso, Sikkeland, Larsh et Latimer ont annoncé la découverte de l'élément n. 103 qu'ils ont appelé lawrencium (Lr). Au

grand cyclotron de Berkeley ces chercheurs ont soumis 3 mg d'un mélange d'isotopes de californium comme cible au bombardement par des noyaux de bore ($B^{10}$ et $B^{11}$) de 10,3 MeV. Ils ont constaté la naissance d'un émetteur de particules alpha de 8,6 MeV et de période égale à $8 \pm 2$ s. Les calculs les ont amenés à conclure qu'il se formait un isotope de l'élément n. 103 de nombre de masse égal à 257. Plus tard on a obtenu également un isotope de plus longue période (35 s): $_{103}Lr^{256}$.

En 1966 Flerov, Drouine, Zvara et al. (Institut uni de recherches nucléaires, à Doubna) ont synthétisé les premiers atomes de l'élément n. 104. Ils ont irradié au cyclotron une préparation de plutonium-242 par des ions de néon-22 de 115 MeV. Ils réalisaient ainsi la réaction nucléaire suivante: $Pu^{242}(_{10}Ne^{22}, 4n)\ 104^{260}$. L'isotope ainsi préparé subissait une désintégration spontanée de période égale à 0,3 s. On le détectait par les traces que forment dans le verre ou le mica les fragments de sa fission. Son identification chimique était effectuée d'après la volatilité de ses composés chlorés (voir plus bas). L'élément n. 104 a reçu le nom de Kourtchatovium (Ku).

Ainsi à l'heure actuelle on connaît 12 éléments transuraniens dont les numéros atomiques s'échelonnent de 93 à 104. Fait remarquable: leurs premiers isotopes que l'on a réussi à isoler étaient généralement des corps de période courte. Ensuite on trouvait des procédés de préparation d'isotopes de période plus longue (table 4). On peut penser que cette règle s'appliquera également aux transuraniens les plus éloignés. Le

TABLE IV.

*Isotopes de transuraniens mis en évidence en premier lieu et caractérisés par les périodes les plus longues.*

| Numéro atomique Z | Elément | Isotopes mis en évidence en premier lieu | | Isotopes caractérisés par les périodes les plus longues | |
|---|---|---|---|---|---|
| | | A | Période | A | Période |
| 93 | Np | 239 | 2,3 j | 237 | $2{,}2 \cdot 10^6$ ans |
| 94 | Pu | 238 | 86,4 ans | 244 | $7{,}6 \cdot 10^7$ d° |
| 95 | Am | 241 | 458 ans | 243 | $8 \cdot 10^3$ d° |
| 96 | Cm | 242 | 162,5 j | 247 | $1{,}6 \cdot 10^7$ d° |
| 97 | Bk | 243 | 4,5 h | 247 | $1{,}4 \cdot 10^3$ d° |
| 98 | Cf | 244 | 2,5 mn | 251 | 800 d° |
| 99 | Es | 246 | 7,3 d° | 254 | 480 j |
| 100 | Fm | 254 | 3,2 h | 257 | 95 j |
| 101 | Md | 256 | 30 mn | 258 | 54 j |
| 102 | No (?) | 256 | 8 mn | — | — |
| 103 | Lr | 257 | 8 s | 256 | 35 s |
| 104 | Ku | 260 | 0,3 s | — | — |

procédé essentiel permettant d'obtenir des quantités importantes de transuraniens consiste à irradier dans des piles atomiques soit l'uranium ordinaire ou enrichi en isotope de masse 235, soit le plutonium par un flux de neutrons de haute puissance. Pour certains transuraniens lourds comme le fermium-257 (période = 95 j) le procédé des explosions souterraines qui s'accompagne de très puissants flux de neutrons est également intéressant. Toutefois dans ce cas il faut extraire l'isotope formé d'une masse considérable de roches fondues par l'explosion.

A présent l'ensemble de la production mondiale annuelle de plutonium se chiffre par quelques tonnes. Le neptunium qui est un sous-produit de la production de plutonium s'obtient par des dizaines de kilogrammes. L'américium est accessible par kilogrammes, le curium — par des dizaines et des centaines de grammes. On a isolé des milligrammes de berkelium et de californium, des microgrammes d'einsteinium et de fermium. Le mendélévium (Z = 101), l'élément n. 102 et le lawrencium (Z = 103) sont étudiés à l'échelle traceur. Dès à présent on peut poser le problème de l'extension des recherches scientifiques et de la mise en œuvre de nombreux transuraniens.

La position de ces éléments dans le système périodique est étroitement liée à la constitution de leurs atomes ainsi qu'à leur valence.

La théorie de la constitution des atomes prévoit qu'au début de la IVme grande période du système de Mendéléev la couche profonde 5f, analogue à la couche 4f qui est formée dans la famille des lanthanides, doit se compléter d'électrons.

En 1945 Seaborg émit l'hypothèse que ce complètement commence après l'actinium ce qui a pour effet de former le groupe ment d'éléments de nombres atomiques 90 à 103 apparenté aux lanthanides et nommé actinides. La théorie des actinides prévoyait une analogie entre les éléments correspondants des familles des lanthanides et des actinides. Toutefois les questions de valence des actinides se sont trouvées être plus compliquées. Pour le thorium, le protactinium et l'uranium les composés les plus caractéristiques répondent à la valence supérieure indiquée par les numéros des groupes où les avait placés Mendéléev — IV, V et VI respectivement.

Les recherches spectrales de Meggers (1947) ont montré que les premiers électrons 5f ne font probablement leur apparition qu'à partir du protactinium. Les mesures cristallographiques de Zachariasen (1954) ont même conduit à cette conclusion que le thorium, le protactinium et l'uranium n'ont pas d'électrons 5f, alors que le neptunium métallique ne contient qu'un seul électron 5f. D'autre part les propriétés magnétiques témoignent de la présence d'électrons 5f, à partir de l'uranium. Il est probable que l'énergie de liaison des électrons 5f et 6d dans les atomes

des actinides a des valeurs voisines. En outre cette énergie est probablement inférieure à celle des électrons 4f des lanthanides.

La table 5 résume les renseignements dont on dispose actuellement sur la constitution des atomes des actinides. Il faut toutefois remarquer

TABLE V.

*Structure des couches électroniques des atomes d'actinides.*

| Elément | Numéro atomique | Niveaux d'énergie et groupes d'électrons dans les atomes | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n = 1 | n = 2 | n = 3 | n = 4 | n = 5 | | n = 6 | | | n = 7 |
| | | K | L | M | N | O | | P | | | Q |
| | | s | s, p | s, p, d | s, p, d, f | s, p, d | f | s | p | d | s |
| Ac | 89 | 2 | 8 | 18 | 32 | 18 | — | 2 | 6 | 1 | 2 |
| Th | 90 | 2 | 8 | 18 | 32 | 18 | — | 2 | 6 | 2 | 2 |
| Pa | 91 | 2 | 8 | 18 | 32 | 18 | 2 | 2 | 6 | 1 | 2 |
| U | 92 | 2 | 8 | 18 | 32 | 18 | 3 | 2 | 6 | 1 | 2 |
| Np | 93 | 2 | 8 | 18 | 32 | 18 | 4 | 2 | 6 | 1 | 2 |
| Pu | 94 | 2 | 8 | 18 | 32 | 18 | 6 | 2 | 6 | — | 2 |
| Am | 95 | 2 | 8 | 18 | 32 | 18 | 7 | 2 | 6 | — | 2 |
| Cm | 96 | 2 | 8 | 18 | 32 | 18 | 7 | 2 | 6 | 1 | 2 |
| Bk | 97 | 2 | 8 | 18 | 32 | 18 | 9 | 2 | 6 | — | 2 |
| Cf | 98 | 2 | 8 | 18 | 32 | 18 | 10 | 2 | 6 | — | 2 |
| Es | 99 | 2 | 8 | 18 | 32 | 18 | 11 | 2 | 6 | — | 2 |
| Fm | 100 | 2 | 8 | 18 | 32 | 18 | 12 | 2 | 6 | — | 2 |
| Md | 101 | 2 | 8 | 18 | 32 | 18 | 13 | 2 | 6 | — | 2 |
| No | 102 | 2 | 8 | 18 | 32 | 18 | 14 | 2 | 6 | — | 2 |
| Lr | 103 | 2 | 8 | 18 | 32 | 18 | 14 | 2 | 6 | 1 | 2 |

que pour beaucoup d'éléments, et surtout pour les éléments ultérieurs de la famille des actinides, ces données sont hypothétiques et n'ont pas pu encore être confirmées par l'expérience.

Dès les études préliminaires du neptunium et du plutonium il a été établi que ces éléments avaient des valences différentes, s'échelonnant de 6 à 3, le neptunium étant caractérisé essentiellement par la valence 5 et le plutonium par la valence 4. On avait supposé que tous les autres actinides seraient trivalents. Mais assez rapidement on avait obtenu des composés d'américium dans lesquels cet élément présentait les valences 4,5 et 6. D'autre part on avait préparé des composés de curium et de berkélium tétravalents. Les valences des lanthanides et des actinides sont comparées dans la table 6.

Récemment Krot et Guelman (1967) ont fait une importante découverte: ils ont obtenu le neptunium et le plutonium à l'état heptavalent.

TABLE VI.

*Valences des lanthanides et des actinides.*

| Lanthanides | | | Actinides | | |
|---|---|---|---|---|---|
| Symbole chimique | Numéro atomique | Valence observée | Valence observée | Numéro atomique | Symbole chimique |
| Ce | 58 | $\underline{3}$, 4 | 3, $\underline{4}$ | 90 | Th |
| Pr | 59 | $\underline{3}$, 4 | 3, 4, $\underline{5}$ | 91 | Pa |
| Nd | 60 | 3 | 3, 4, 5, $\underline{6}$ | 92 | U |
| Pm | 61 | 3 | 3, 4, $\underline{5}$, 6, 7 | 93 | Np |
| Sm | 62 | 2, $\underline{3}$ | 3, $\underline{4}$, 5, 6, 7 | 94 | Pu |
| Eu | 63 | 2, $\underline{3}$ | (2), $\underline{3}$, 4, 5, 6 | 95 | Am |
| Gd | 64 | 3 | $\underline{3}$, 4 | 96 | Cm |
| Tb | 65 | $\underline{3}$, 4 | $\underline{3}$, 4 | 97 | Bk |
| Dy | 66 | 3 | 3, (4) | 98 | Cf |
| Ho | 67 | 3 | 3 | 99 | Es |
| Er | 68 | 3 | 3 | 100 | Fm |
| Tu | 69 | 3 | 2, $\underline{3}$ | 101 | Md |
| Yb | 70 | 2, $\underline{3}$ | $\underline{2}$, 3 | 102 | No (?) |
| Lu | 71 | 3 | 3 | 103 | Lr |

Si l'on oxyde les suspensions dans l'eau des neptunates (VI) et des plutonates (VI) — $K_2NpO_4$ et $K_2PuO_4$ par l'ozone en milieu fortement alcalin, les précipités se dissolvent progressivement en formant des solutions vertes foncées des neptunates (VII) et des plutonates (VII) comme par exemple:

$$2K_2NpO_4 + O_3 + 2KOH = 2K_3NpO_5 + O_2 + H_2O\,.$$

A partir de ces solutions on a obtenu à l'état solide plusieurs composés de neptunium et de plutonium heptavalents:

$$[Co(NH_3)_6]NpO_5 \cdot 3H_2O\,,\ [Pt(NH_3)_5Cl]NpO_5\,,$$
$$Si_3(NpO_5)_2 \cdot nH_2O\,,\ Ba_3(NpO_5)_2 \cdot nH_2O\,,\ Ba_3(PuO_5)_2 \cdot nH_2O\,.$$

Les composés du neptunium (VII) sont verts foncés, ceux de plutonium (VII) ont une coloration brun-noirâtre. Ils manifestent de fortes propriétés oxydantes, surtout le plutonium heptavalent.

L'oxydation du neptunium et du plutonium jusqu'à l'état heptavalent peut se faire non seulement par l'ozone, mais aussi par l'hypochlorite, l'hypobromite, par les composés du xénon et autres oxydants actifs, mais toujours en milieu fortement alcalin.

Récemment les techniques de porteurs ont été appliquées à l'étude des états valents des actinides ultérieurs de la plus courte période qui étaient utilisés à l'échelle traceur ou bien sous forme d'atomes individuels [6]. L'état bivalent a été déterminé par capture, avec précipité de $BaSO_4$, tandis que les états tri- et tétravalents ont été déterminés par extraction à la méthylisobutylcétone ou avec d'autres solvants. Les essais ont montré qu'en solutions aqueuses le mendélévium ($Z = 101$) était trivalent mais qu'il pouvait être facilement réduit en bivalent par de la poudre de zinc, le chrome bivalent ou autres réducteurs. C'est par ces propriétés que le mendélévium se distingue de son analogue lanthanidique formel qu'est le thulium que l'on ne connaît pas à l'état bivalent.

L'élément n. 102 en solutions dans l'acide nitrique n'a été mis exclusivement en évidence que sous sa forme bivalente, et pour le faire passer à l'état trivalent il faut utiliser des oxydants forts. Là encore on observe des différences sensibles avec l'ytterbium, analogue formel lanthanidique.

Des essais préliminaires effectués sur un petit nombre d'atomes du lawrencium ($Z = 103$) ont permis de conclure que cet élément se présentait d'une façon constante comme trivalent bien que ses réactions de réduction ou d'oxydation soient possibles. Le lawrencium termine la famille des actinides et il devrait manifester des analogies avec le lutécium qui est caractérisé par la valence 3.

Les divergences observées entre les propriétés des lanthanides et des actinides et, en premier lieu des valences qu'ils manifestent, ne sont pas surprenantes. Elles s'expliquent entièrement du point de vue de la loi périodique de Mendéléev. Dans chaque groupe du système périodique, au fur et à mesure que les numéros atomiques augmentent, les éléments analogues sont caractérisés par une modification déterminée de ses propriétés physiques et chimiques. Cela s'observe non seulement pour quelques éléments pris separés, mais encore pour leurs groupements. On pourra prendre comme exemple les valeurs des potentiels d'ionisation (fig. 4).

On sait que dans chaque période de la classification de Mendéléev la valeur maximale du potentiel d'ionisation correspond au gaz inerte alors que la valeur minimale — à l'élément alcalin. Pour les éléments aux limites des deux espèces les potentiels d'ionisation diminuent au fur et à mesure que les numéros atomiques croissent se qui est incontestablement lié à l'augmentation des rayons atomiques du fait du remplissage des couches électroniques de plus en plus reculées des atomes. Autre fait crucial: la différence entre les potentiels d'ionisation du gaz noble et de l'élément alcalin tombe sensiblement à la fin du système périodique. Cela explique l'activité chimique accrue des gaz inertes lourds comme le xénon et le radon ainsi que l'aptitude des actinides proches et moyens

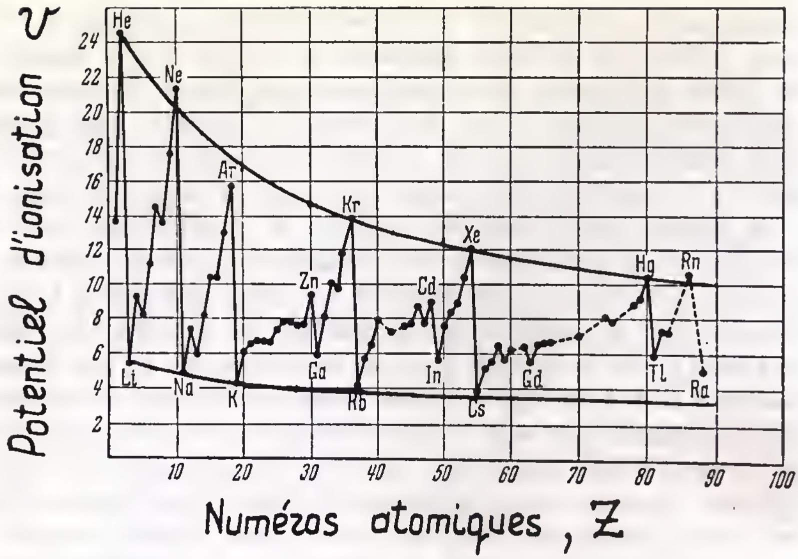


Fig. 4.

Potentiels d'ionisation des éléments (pour le premier électron).

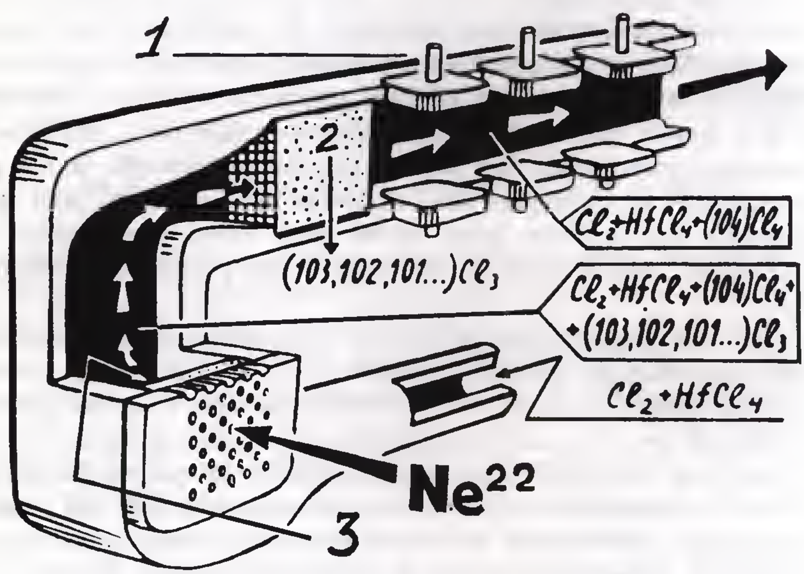


Fig. 5.

Schéma de l'appareil pour la détermination de l'état de valence de l'élément n. 104

1. les compteurs de fission, 2. le filtre, 3. la cible.

de manifester des valences élevées et variées. On est en droit de penser que les actinides éloignés pourront donner, eux aussi, des composés de valence élevée bien que dans les conditions ordinaires leurs valences les plus caractéristiques soient 3 et 2.

La valence du kourtchatovium, l'élément n. 104, offre un grand intérêt. Ce corps ne se rapporte plus aux actinides, il doit être analogue à l'hafnium et thorium et posséder la valence 4. Zvara et collaborateurs [6] à l'Institut Uni des recherches nucléaires (à Doubna) ont montré par une méthode élégante que la valence du kourtchatovium différait effectivement de celle des lanthanides et des actinides ultérieurs (fig. 5). Les produits de la réaction nucléaire qui mène à la formation des noyaux de $_{104}Ku^{260}$ entraînés par un courant d'azote et de chlore additionnés de $HfCl_4$ et de $NbCl_5$ traversaient un filtre spécial qui retenait à 350° les chlorures moins volatiles des lanthanides et des éléments n. 101, 102, 103. Ensuite les compteurs de fission spontanée détectaient toujours l'élément n. 104 prouvant qu'il différait des lanthanides et des actinides.

Au point de vue formel l'élément n. 105 doit être analogue au tantale, l'élément n. 106 — au tungstène etc. Cependant, vu la similitude au point de vue énergétique des électrons 5f et 6d, on peut s'attendre à ce que les premiers transactinides (Z de 104 à 106) manifestent une valence anormalement élevée tout comme les éléments du sous-groupe de cuivre, dont la valence élevée est due à la proximité des niveaux d'énergie des électrons s-d extérieurs.

***

Une contribution importante au système périodique fut l'étude des propriétés chimiques des éléments du groupe 0. Au cours des années trente, utilisant le procédé de cocristallisation avec l'hydrate de l'anhydride sulfureux $SO_2 \cdot 6H_2O$, Nikitine a montré que le radon et certains autres gaz inertes forment des hexahydrates $Rn \cdot 6H_2O$, $Ar \cdot 6H_2O$, $Ne \cdot 6H_2O$ etc. Plus tard il a établi que le radon réagissait également avec le toluène, le parachlorophénol et autres corps organiques en formant des composés de formules générales $Rn \cdot 2C_6H_5CH_3$, $Rn \cdot 3ClC_6H_4OH$ qui ont un caractère de composés de coordination.

En 1962 Bartlett a obtenu le premier composé du gaz inerte xénon formé par liaison de valence. Il a constaté que l'hexafluorure de platine $PtF_6$ qui est un oxydant très puissants est capable d'oxyder le xénon en composé de formule $Xe^+[PtF_6]^-$. Sous l'action de l'eau ce composé est hydrolysé:

$$2XePtF_6 + 6H_2O = 2Xe + O_2 + 2PtO_2 + 12HF\,.$$

Après cette découverte d'autres auteurs ont obtenu un composé fluoré de xénon $XeF_4$ par réaction directe entre le fluor et le xénon à 400° suivie d'un refroidissement rapide jusqu'à la température ordinarie. Le tétrafluorure de xénon est stable à la température ordinaire. Il est hydrolysé par l'eau

$$XeF_4 + 2H_2O = Xe + O_2 + 4HF .$$

Par action du rayonnement ultraviolet sur un mélange de xénon et de fluor on a préparé le difluorure $XeF_2$. En présence de fluor en excès, sous des pressions élevées (60 à 70 atm) il se forme aussi $XeF_6$. Ce composé, hydrolysé par l'eau, donne un produit solide, non volatil que l'on a identifié comme le trioxyde de xénon $XeO_3$. Le trioxyde de xénon est stable à la lumière et à l'air, mais devient déliquescent en présence de l'humidité. $XeO_3$ explose sous l'effet de la chaleur. Il est sujet également à une disproportionation qui aboutit au tétroxyde de xénon:

$$4XeO_3 = 3XeO4 + Xe .$$

Les sels $CsHXeO_4$, $BaXeO_4$ appelés xénonates correspondent au trioxyde de xénon, tandis que les perxénonates ($Na_4XeO_6 \cdot 8H_2O$, $K_4XeO_6 \cdot 9H_2O$ etc.) répondent au tétroxyde de xénon.

On trouvera ci-après les renseignements sur les composés simples du xénon connus actuellement:

Valence

| 2 | 4 | 6 | 8 |
|---|---|---|---|
| $XeF_2$ | $XeF_4$ | $XeF_6$ | $[XeF_8]$ |
| $XeCl_2$ | $XeOF_2$ | $XeOF_4$ | $XeO_4$ |
| $XeO$ | $XeO_2$ | $XeO_2F_2$ | |
| | | $XeO_3$ | |

Les fluorures de xénon sont des corps cristallins blancs qui se décomposent sous l'action de la chaleur. Ils manifestent de fortes propriétés oxydantes. C'est ainsi que le mélange $XeF_4 + XeF_6$ enflamme le méthanol et la solution aqueuse d'ammoniaque, transforme le manganèse bivalent en acide permanganique. Grâce aux fluorures de xénon on a réussi pour la première fois à préparer les perbromates, sels de l'acide perbromique.

On a établi également qu'il y avait interaction entre la radon et le fluor. Il est probable que les combinaisons chimiques du radon les seront plus stables parmi celles des gaz inertes. Toutefois la haute

radio-activité de cet élément constitue un obstacle pour l'étude de ses propriétés chimiques. Pour le crypton on n'a obtenu qu'un seul composé — $KrF_2$ instable à la température ordinaire. En partant des considérations théoriques on peut penser que la formation des composés chimiques d'argon, de néon et d'hélium est peu probable.

Dès les premières décennies de la loi périodique on a commencé à comparer les propriétés physiques et chimiques des éléments et de leurs composés à la position de ces éléments dans la classification périodique. Depuis quelques années on attache de plus en plus l'attention à la recherche des relations quantitatives dans ce domaine. A titre d'exemple on pourrait citer les travaux suivants.

Somayadjulu et Palit (1957) ont étudié la relation entre le point d'ébullition de divers dérivés halogénés et les dimensions des atomes qui les composent. Ils ont trouvé que le point d'ébullition des termes d'une certaine série de dérivés halogénés, notamment des combinaisons interhalogénées dépend linéairement de la superficie des atomes d'halogènes calculée pour la molécule en question. On peut calculer le point d'ébullition par la formule suivante:

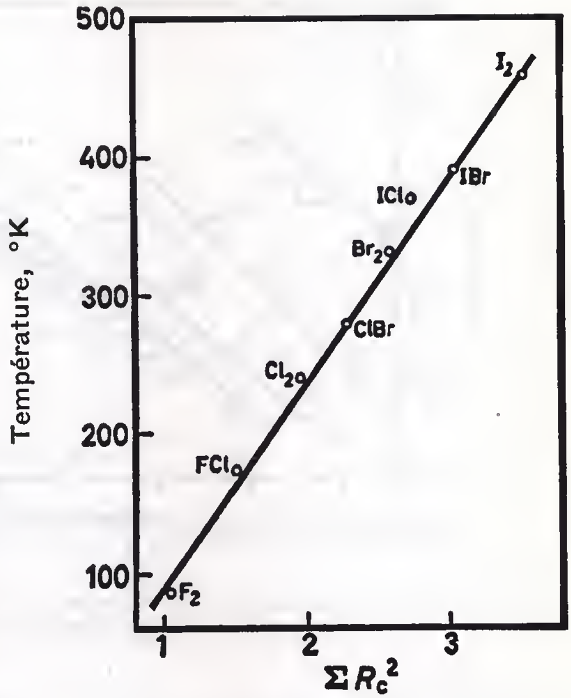


Fig. 6.

Relation entre les points d'ébullition des composés diatomiques interhalogénés et des valeurs des rayons de convalence des atomes d'halogènes.

$$Eb = a_1 \sum R_c^2 + b \,.$$

Eb étant le point d'ébullition (°K); $R_c$ — les rayons covalentes des atomes d'halogènes dans la molécule; $a_1$ et $b$ — des constantes.

La fig. 6 montre l'applicabilité de cette formule à la détermination du point d'ébullition des combinaisons interhalogénées du type $X_2$, alors

que la fig. 7 indique son applicabilité aux points d'ébullition de quatre séries de dérivés halogénés de divers types.

Szabo et Lakatos (1952) ont émis l'hypothèse que les propriétés physiques d'éléments libres (leurs points de fusion et d'ébullition, leurs chaleurs de sublimation) dépendent non seulement de la valeur des numéros atomiques, mais encore de la distribution fine des électrons entre

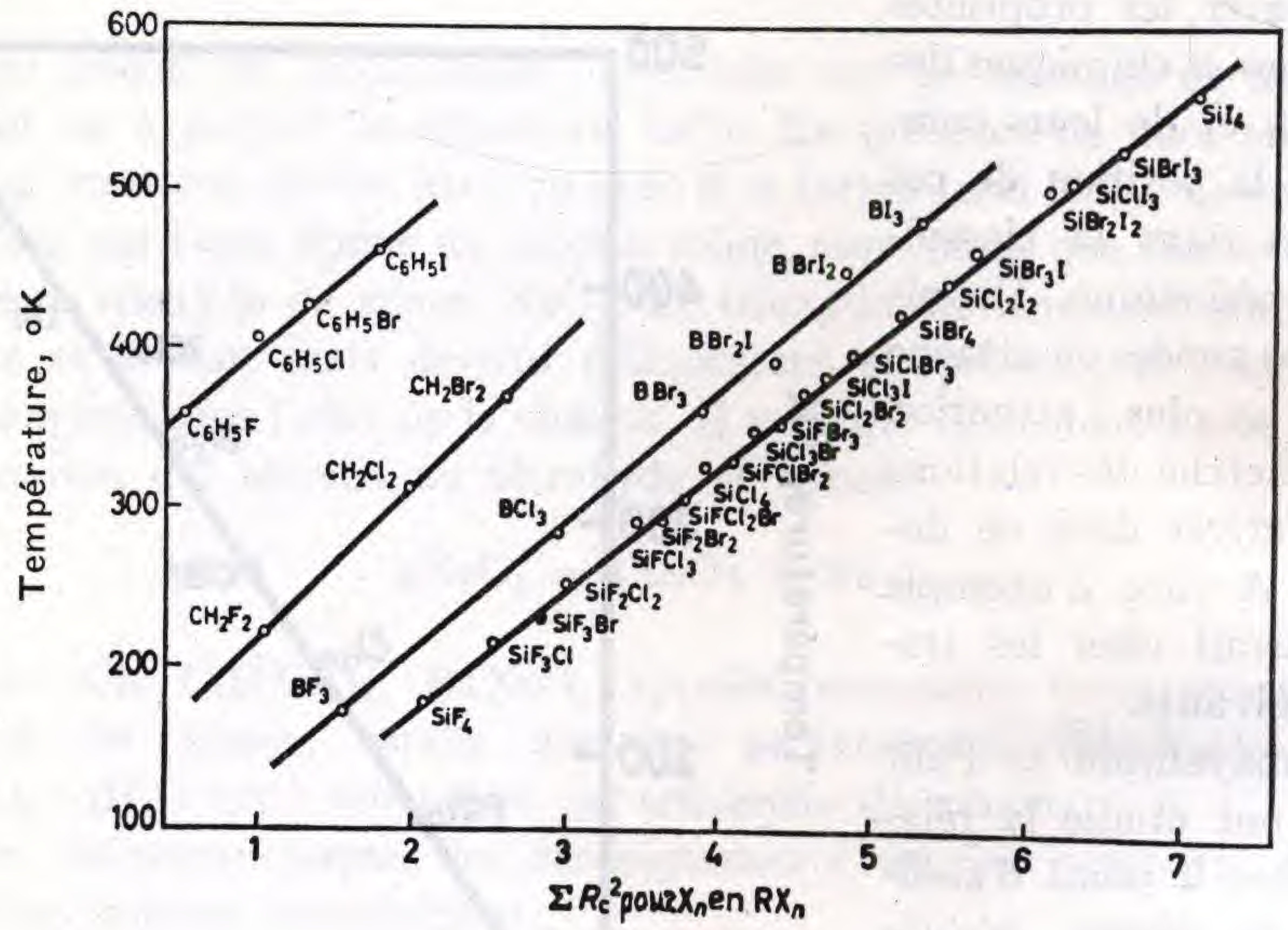


Fig. 7.

Relation entre les points d'ébullition de divers halogénures et les valeurs des rayons covalents des atomes d'halogènes.

les sous-niveaux *s*, *p* et *d*. Cela conduit à une périodicité complémentaire à l'intérieur de chaque période de la classification de Mendéléiev. La fig. 8 montre ce phénomène pour les points de fusion des éléments de transition de trois grandes périodes. Les points représentatifs des points de fusion d'éléments analogues se placent, en règle générale, sur des droites. Szabo et Lakatos ont proposé les équations suivantes pour le calcul des points de fusion des éléments:

$$T = a_1 e^{-b_1^2(d-4)^2} + a' e^{-b'^2(d-5)^2}(n - n_5) \qquad \text{si } d \leqq 5$$

ou

$$T = a_2 e^{-b_2^2(d-6)^2} + a' e^{-b''^2(d-5^2)}(n - n_5) \qquad \text{si } d \geqq 5$$

$T$ étant le point de fusion; $a_1$, $a_2$, $b_1$, $b_2$ — des constantes de la courbe périodique; $a'$, $b'$, $b''$ des constantes qui entrent en fonction de la pente

de la courbe; $n$ — le nombre quantique principal; $d$ — le nombre d'électrons $d$, si tout le calcul se fonde sur les propriétés des éléments de la cinquième période ($n_5$). Les valeurs calculées s'écartaient des valeurs expérimentales de 4% en moyenne.

An. N. Nesmeyanov et N. E. Khandamirova (1960) ont trouvé des relations quantitatives entre le chaleur de sublimation des éléments

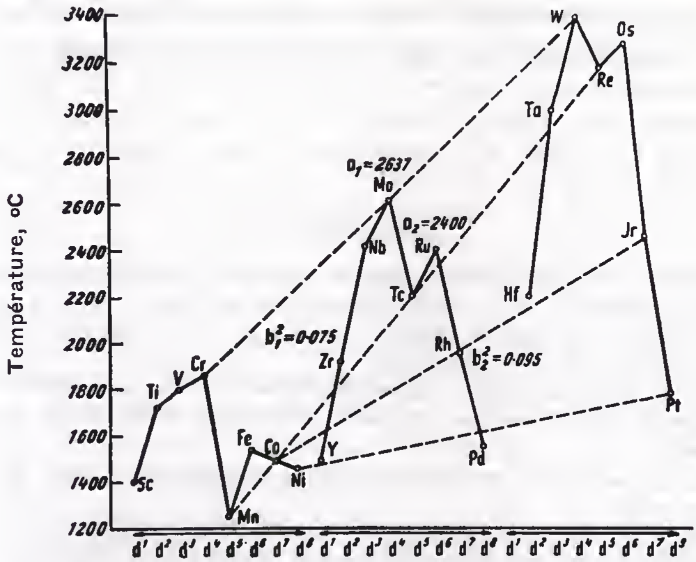


Fig. 8.

Points de fusion des éléments de transition.

($\Delta H^{\circ}_{298}$) et leur position dans le système périodique. En considérant l'énergie de liaison réticulaire du corps solide comme une fonction de deux paramètres fondamentaux — la distance intératiomique $r$ et la masse atomique $A$ ces auteurs ont établi que la grandeur $\frac{\Delta H^{\circ}_{298} \cdot A}{r}$ est une fonction linéaire de la masse atomique dans les limites de chaque sous-groupe du système périodique. Utilisant des graphiques appropriés on peut calculer la chaleur de sublimation. Dans la majorité des cas on a constaté que les valeurs calculées coincidaient d'une façon satisfaisante avec les valeurs expérimentales. On observe des écarts pour les sous-groupes du cuivre et du zinc ce qui s'explique par la pénétration des électrons $s$ sous la protection des électrons $d$ et la diminution relative des dimensions des atomes qui lui est connexe.

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Un siècle après la découverte de la loi périodique on peut dresser le bilan de ses applications en chimie, physique et dans plusieurs branches connexes du savoir. Cette loi a non seulement expliqué beaucoup de faits connus, mais fit prévoir aussi des phénomènes nouveaux, souvent insoupçonnés. Cependant les succès obtenus sont loin d'indiquer que les possibilités de la loi périodique sont épuisées. Elle servira toujours aux savants de fil conducteur vers d'autres découvertes. Le nom de son auteur, le grand savant russe Dmitri Mendéléev, sera gravé à perpétuité dans le mémorial de la science et il appartient à tout le monde, à l'humanité.

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EMILIO SEGRÉ (*)

# The Completion and Extension of the Periodic System of the Elements.

The study of chemical elements, whether they were called so or not, has been one of the central themes in the investigation of the world around us from remote antiquity and it would be most interesting to retrace the development of the concept of element from the origin to now. Unfortunately this is impossible in our limited time. I will only point out that from the beginning of scientific chemistry, that is from about 1700 to now, the concept of what is to be called a chemical element has evolved. Up to 1900 one used an operative definition about as follows: « Element is what may not be further decomposed by chemical means ». This is the way in which Mendeleev expresses himself in 1904, « One has to distinguish between simple bodies and elements because the conception of a simple body implies the idea of an impossibility of transforming certain bodies into other bodies while the conception of a chemical element is merely determined by the desire of diminishing the number of substances which are required for explaining the great variety of the latter ». On the basis of this definition of element, the chemical atomic theory was developed in the 19th century. The definition of element was the one used by Mendeleev.

The discovery of elements is hence strictly connected with technical development of analytical methods because there is always the possibility that a substance may be further decomposed with better methods. Figure 1 gives the chronological list of the discovery of elements. The first two lines contain the elements known to antiquity and those added in the middle ages up to about 1700. One has to wait until about 1770 to see a vigorous development of chemistry in modern sense. The discoveries up to 1800 are mainly the work of metallurgists, alchemists and pharmacists, (in English the word chymist and pharmacist are not as well distinguished as in Italian), and they are connected, as I said before,

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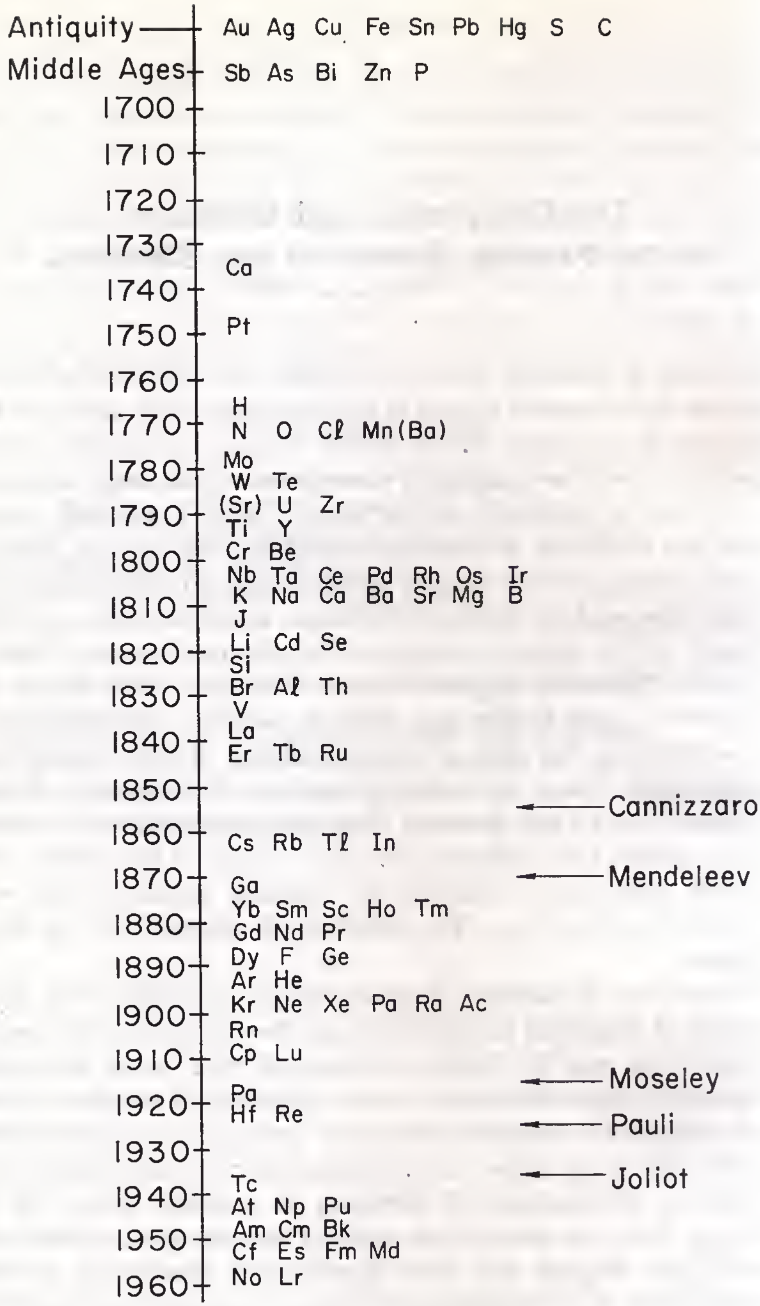



Fig. 1.

Chronological list of the discovery of the elements.

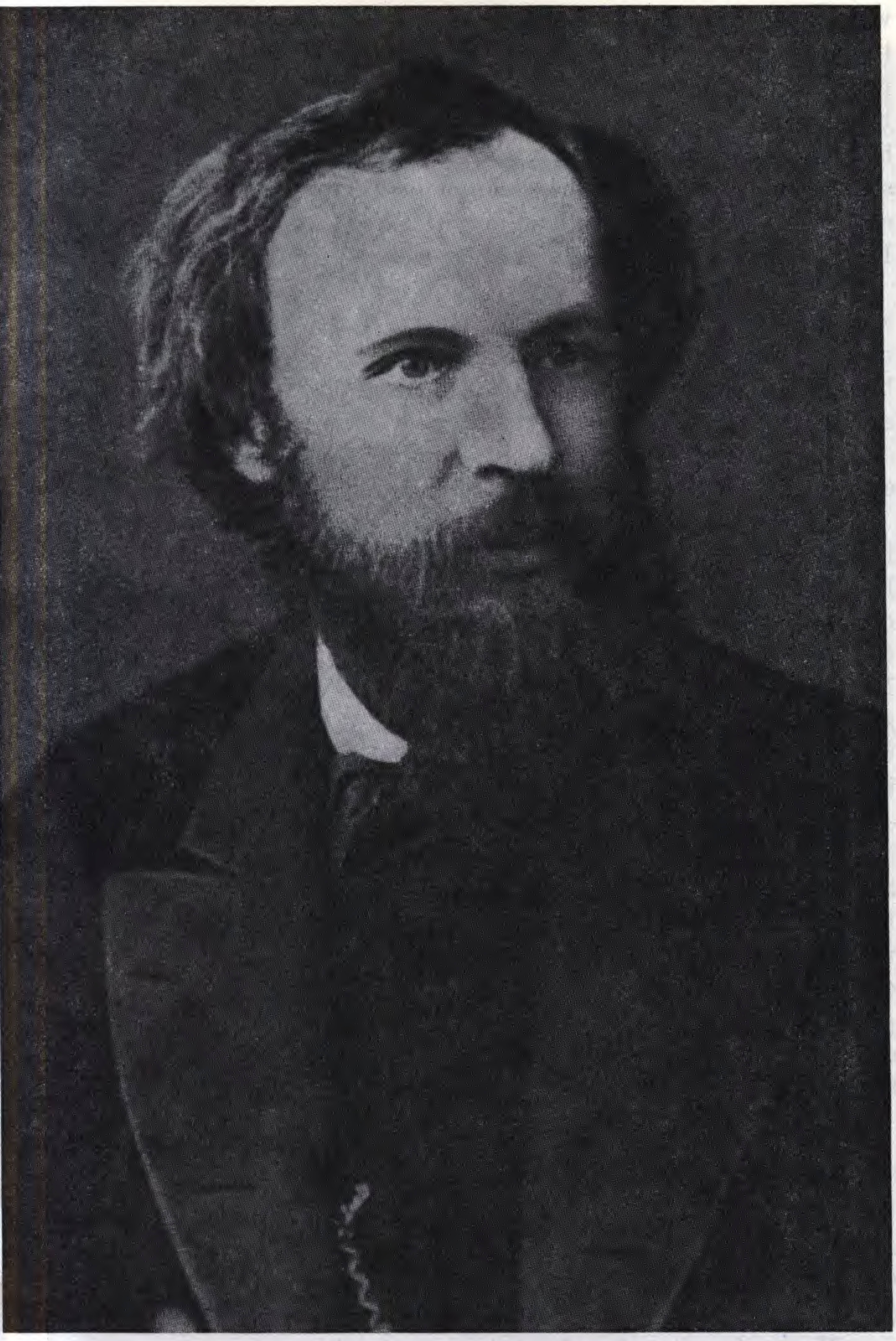


Fig. 2.
Mendeleev at the time of his first publication on the periodic system.

with analytical and preparative techniques. For instance, oxygen and the other gases are the fruits of the techniques for manipulating gases or pneumatical techniques as one used to call them, and those techniques by killing the phlogiston theory together with the introduction of the balance in chemistry put that science on a quantitative basis. Potassium, sodium, and others are the children of electrolysis; similarly rubidium, cesium, thallium, and indium are the products of spectrum analysis. Radium and polonium are the products of the discovery of radioactivity, etc.

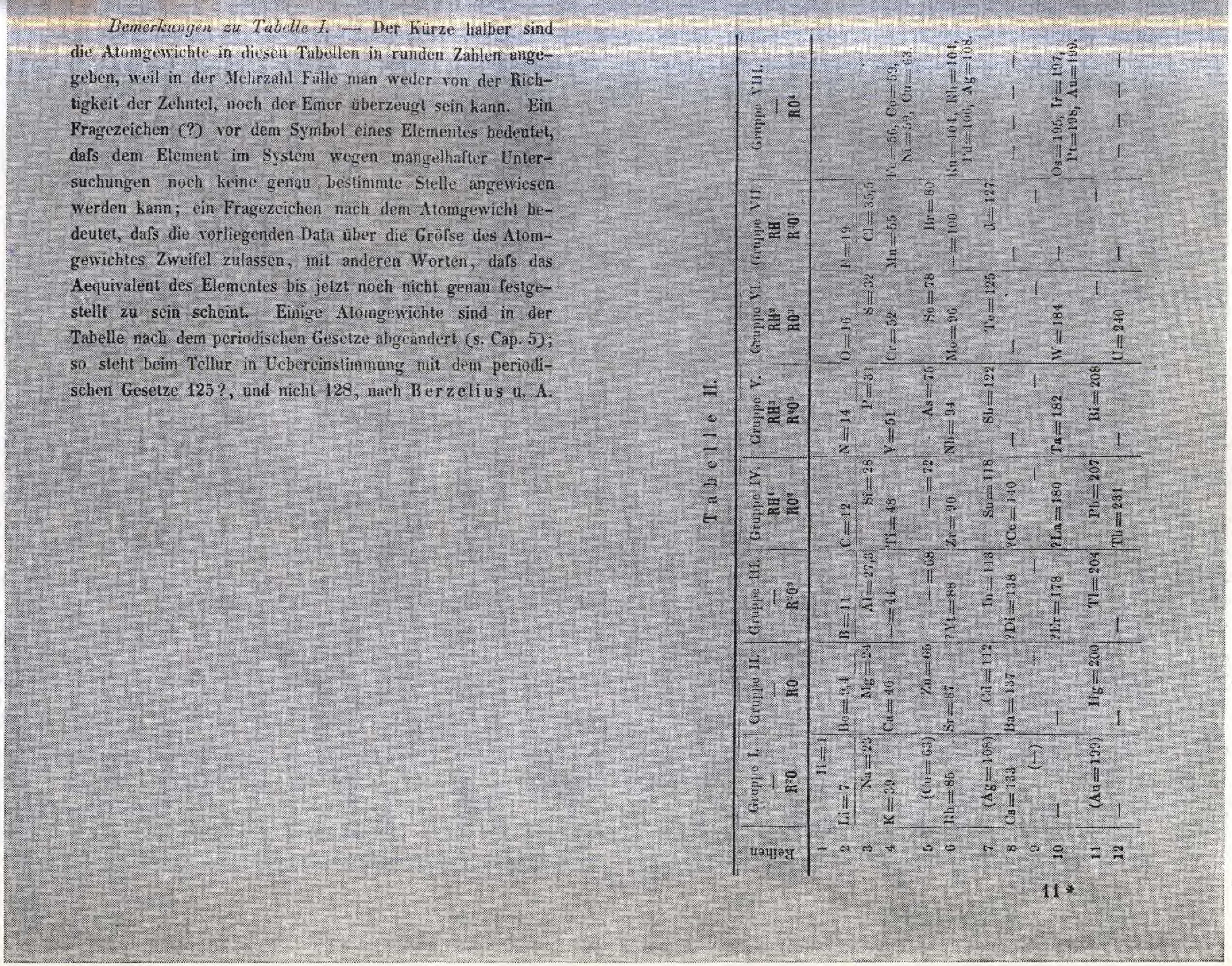
Dalton, Gay Lussac, Avogadro and finally Cannizzaro established on a solid basis the concept of atomic weight. It is somewhat remarkable that one had to wait so late to have a real reliable scale of atomic weights, but there were both experimental and theoretical reasons which made this endeavor quite difficult and up to about 1860 one did not have a table of atomic weights having a precision of about 1% and without many gross errors. At that time, in 1860, it contained about 60 elements.

By 1865 already several regularities had appeared and elements had been grouped in families with similar properties: the alkali metals, the halogens, the earths, the alkaline earths, etc. The idea of a classification of the elements was thus natural and indeed there have been several attempts in that direction among which one has to mention those of Lothar Mayer, J. A. R. Newlands, W. Odling and several others. However, the greatest success was achieved by Mendeleev. Born in Siberia in 1834, the fourteenth son of a professor in a gymnasium and of an exceptionally intelligent woman which in turn came from a family of industrialists — if one could speak of industry in the Siberia of that time — he studied chemistry at St. Petersburg and then in Heidelberg. In 1869, a hundred years ago, he published his first paper on the periodic system. He was then 34 years old, fig. 2. In this paper he assumes the atomic weight as the most fundamental property of an element and after having ordered the elements in the order of increasing atomic weight, he finds periodical changes of the chemical properties. His most important conclusions are summarized in a page and in a table. I quote from a translation of his original papers published in 1871, fig. 3.

1. The elements, if arranged according to their atomic weights, show a distinct periodicity of their properties.

2. Elements exhibiting similarities in their chemical behavior have atomic weights which are approximately equal (as in the case of Pt, Ir, Os) or they possess atomic weights which increase in a uniform manner (as in the case of *K*, *Rb*, *Cs*).

The uniformity of such an increase in the various groups remained hidden to previous observers since in their calculations they did not make



*Bemerkungen zu Tabelle I.* — Der Kürze halber sind die Atomgewichte in diesen Tabellen in runden Zahlen angegeben, weil in der Mehrzahl Fälle man weder von der Richtigkeit der Zehntel, noch der Einer überzeugt sein kann. Ein Fragezeichen (?) vor dem Symbol eines Elementes bedeutet, dafs dem Element im System wegen mangelhafter Untersuchungen noch keine genau bestimmte Stelle angewiesen werden kann; ein Fragezeichen nach dem Atomgewicht bedeutet, dafs die vorliegenden Data über die Gröfse des Atomgewichtes Zweifel zulassen, mit anderen Worten, dafs das Aequivalent des Elementes bis jetzt noch nicht genau festgestellt zu sein scheint. Einige Atomgewichte sind in der Tabelle nach dem periodischen Gesetze abgeändert (s. Cap. 5); so steht beim Tellur in Uebereinstimmung mit dem periodischen Gesetze 125?, und nicht 128, nach Berzelius u. A.

T a b e l l e II.

| Reihen | Gruppe I. — $R^2O$ | Gruppe II. — RO | Gruppe III. — $R^2O^3$ | Gruppe IV. $RH^4$ $RO^2$ | Gruppe V. $RH^3$ $R^2O^5$ | Gruppe VI. $RH^2$ $RO^3$ | Gruppe VII. RH $R^2O^7$ | Gruppe VIII. — $RO^4$ |
|---|---|---|---|---|---|---|---|---|
| 1 | H=1 | | | | | | | |
| 2 | Li=7 | Be=9,4 | B=11 | C=12 | N=14 | O=16 | F=19 | |
| 3 | Na=23 | Mg=24 | Al=27,3 | Si=28 | P=31 | S=32 | Cl=35,5 | |
| 4 | K=39 | Ca=40 | —=44 | Ti=48 | V=51 | Cr=52 | Mn=55 | Fe=56, Co=59, Ni=59, Cu=63. |
| 5 | (Cu=63) | Zn=65 | —=68 | —=72 | As=75 | Se=78 | Br=80 | |
| 6 | Rb=85 | Sr=87 | ?Yt=88 | Zr=90 | Nb=94 | Mo=96 | —=100 | Ru=104, Rh=104, Pd=106, Ag=108. |
| 7 | (Ag=108) | Cd=112 | In=113 | Sn=118 | Sb=122 | Te=125 | J=127 | |
| 8 | Cs=133 | Ba=137 | ?Di=138 | ?Ce=140 | — | — | — | — — — — |
| 9 | (—) | — | — | — | — | — | — | |
| 10 | — | — | ?Er=178 | ?La=180 | Ta=182 | W=184 | — | Os=195, Ir=197, Pt=198, Au=199. |
| 11 | (Au=199) | Hg=200 | Tl=204 | Pb=207 | Bi=208 | — | — | |
| 12 | — | — | — | Th=231 | — | U=240 | — | — — — — |

11 *

Fig. 3.
The first periodic system table as given by Mendeleev in 1869.

use of the conclusions drawn by Gerhardt, Regnault, Cannizzaro, and others, by which conclusions the true magnitude of the atomic weights of the elements was determined.

3. The arrangement of elements or of groups of elements according to their atomic weights corresponds to their valencies, as well as, to some extent, to their distinctive chemical properties, a fact which can be clearly seen from the row: *Li, Be, B, C, N, O, F* and which also occurs in the other rows.

4. The bodies most abundantly found in nature possess a small atomic weight; but all elements of small atomic weight are characterized by their distinct properties and are, therefore, typical elements. Hydrogen, being the lightest element, is reasonably to be chosen as the most typical element of all.

5. The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the properties of a compound body; it is therefore necessary in the study of compounds to direct attention not only towards the properties and number of the elements as well as to their mutual behavior, but also towards their atomic weight. Thus, the compounds, e.g., of *S* and *Te*, *Cl* and *I* and of others, present, in spite of all their resemblance, distinct differences.

6. The discovery of numerous unknown elements is still to be expected, for instance, of elements similar to *Al* and *Si* having atomic weights from 65-75.

7. The atomic weight of an element will have to be corrected, eventually, when its analogues become known. Thus, must not the atomic weight of tellurium be 123-126, and not 128?

It was characteristic of Mendeleev how seriously he took his table. He had so much confidence in it that he concluded that several of the atomic weights which had been tabulated must have been in error (Iodine and Tellurium) and also that some elements were missing. Of the missing elements he predicted the atomic weight, the valency, the metallic character, density, several of the most important compounds, etc. He also gave them provisional names like Eka boron (scandium); Eka aluminium (gallium); Eka silicium (germanium). When some years later his prophecies were verified, by the discovery of gallium (Lecoq de Boisbaudran 1875) and scandium (Nilson 1879), he obtained an immense and well justified reputation. If we analyse how Mendeleev had built his table, we find that he had a very deep knowledge of the empirical material. This was his mainstay. He had also a keen intuition, great optimism, and also without any disrespect, a good dose of luck. Certainly in 1869 it would not have been possible to give a rational foundation to the periodic system.

| Rows | Group zero | Group I | Group II | Group III | Group IV | Group V | Group VI | Group VII | Group VIII |
|---|---|---|---|---|---|---|---|---|---|
| 0 | *x* | | | | | | | | |
| 1 | *y* | H=1.008 | | | | | | | |
| 2 | He=4.0 | Li=7.03 | Be=9.1 | B=11.0 | C=12.0 | N=14.04 | O=16.0 | F=19.0 | |
| 3 | Ne=19.9 | Na=23.05 | Mg=24.1 | Al=27.0 | Si=28.4 | P=31.0 | S=32.06 | Cl=35.45 | |
| 4 | Ar=38. | K=39.1 | Ca=40.1 | Sc=44.1 | Ti=48.1 | V=51.4 | Cr=52.1 | Mn=55.0 | Fe=55.9 Co=59<br>Ni=59 (Cu) |
| 5 | | Cu=63.6 | Zn=65.4 | Ga=70.0 | Ge=72.3 | As=75.0 | Se=79 | Br=79.95 | |
| 6 | Kr=81.8 | Rb=85.4 | Sr=87.6 | Y=89.0 | Zr=90.6 | Nb=94.0 | Mo=96.0 | — | Ru=101.7 Rh=103.0<br>Pd=106.5 (Ag) |
| 7 | | Ag=107.9 | Cd=112.4 | In=114.0 | Sn=119.0 | Sb=120.0 | Te=127 | I=127 | |
| 8 | Xe=128 | Cs=132.9 | Ba=137.4 | La=139 | Ce=140 | — | — | — | — — — (—) |
| 9 | | — | — | — | — | — | — | — | |
| 10 | — | — | — | Yb=173 | — | Ta=183 | W=184 | — | Os=191 Ir=193<br>Pt=194.9 (Au) |
| 11 | | Au=197.2 | Hg=200.0 | Tl=204.1 | Pb=206.9 | Bi=208 | — | — | |
| 12 | — | — | Rd=224 | — | Th=232 | — | U=239 | — | |

Fig. 4.

One has only to think that thirty years later there still were distinguished scientists who did not even believe in the existence of atoms. It is also clear that Mendeleev's table could not predict the number of rare earths or anticipate the existence of noble gases. The following fig. 4 shows one of the last periodic tables published by Mendeleev himself in 1904 and finally a modern periodic table (fig. 5). Mendeleev was intellectually a very daring man and he did not hesitate to express radical scientific ideas.

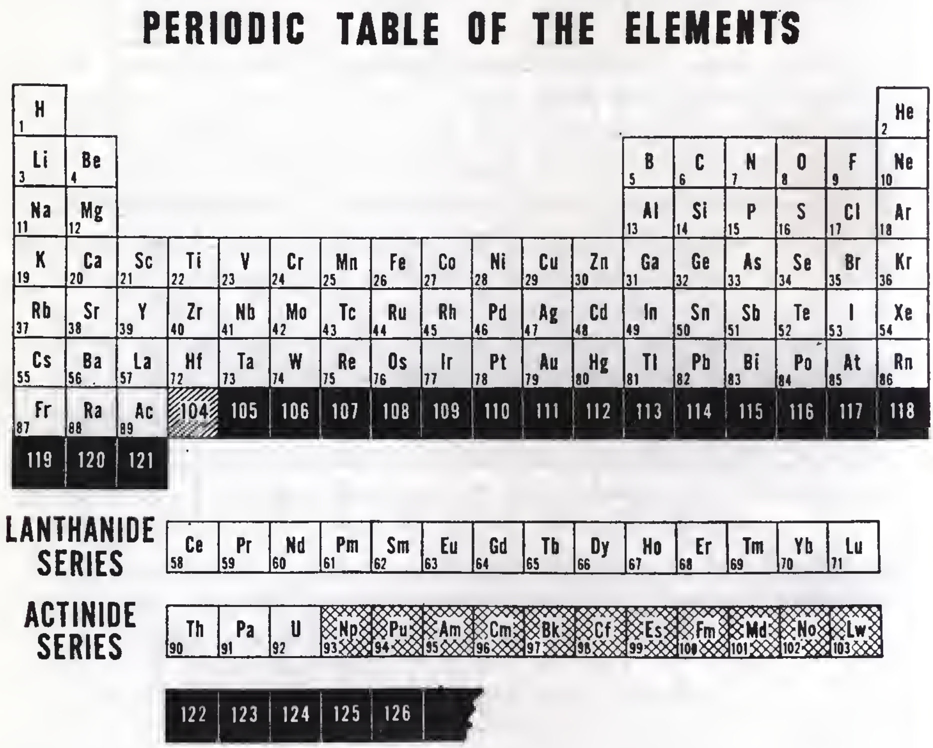



Fig. 5.
A modern periodic system table ([1]).

It is thus no wonder that if we take his later papers, for instance, the one of 1904 quoted above, one finds ideas which are quite wrong, for instance, that there was no evidence that helium was a product of disintegration of radium. The work of Mendeleev, however, because of the daring of its concepts and the influence it has exerted on the development of chemistry, is one of the greatest triumphs of science.

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([1]) The names rutherfordium (RF) and hahnium (Ha) have been proposed for elements 104 and 105. (Note added in proof).

In order to give a solid basis to the genial intuitions of Mendeleev it took about fifty years of work and the development of a complete theory of the atom as one has obtained from quantum mechanics. Among the principal steps one has to remember the discovery of isotopes, of the Rutherford atomic model and of the atomic number by Moseley in 1913, which fixed the order of the elements as given by the number of electrons they contain and also gives a way of measuring this number through the x-ray spectra. Thus what Mendeleev tried to do empirically by using the atomic weights can now be done scientifically and without any ambiguity by using the atomic number. The final step was the discovery of the exclusion principle by Pauli in 1926 which gives the key to establishing the length of the periods of Mendeleev. In spite of all this even now it would not be easy to calculate the properties of all elements from first principles. The transuranics have shown this. While the theoretical foundations of the periodic system were developed, new technical methods have allowed to recognize and discover new elements, thus radioactivity has produced polonium, radium, radon, actinium, protactinium, and x rays have allowed the discovery, in ores, of hafnium and rhenium.

About 1930 there were only a few empty places left in the periodic system. The atomic numbers 43, 61, 85, and 87 were unknown and the system ended at 92. Up to then all the elements had been dug from the earth and those which were missing were hopeless because they do not exist in nature. In fact they are radioactive with a life short compared with geological times and thus even if they existed at the beginning of the world they would have decayed by now.

Thus this would have been the end of the story without the discoveries and the developments of nuclear physics and of nuclear disintegrations and in particular without the discovery of artificial radioactivity by I. Curie and F. Joliot in 1934. Nuclear reactions as first seen by Rutherford give a way of changing $Z$ and thus of transmuting the elements. This is done by bombarding stable nuclei, which are found in nature, with suitable projectiles. For instance; we can write a nuclear reaction:

$$_{13}\mathrm{Al}^{27} + {_0}n^1 \rightarrow {_{11}}\mathrm{Na}^{24} + {_2}\mathrm{He}^4$$

or briefly

$$_{13}\mathrm{Al}^{27}\,(n, \alpha) \rightarrow {_{11}}\mathrm{Na}^{24}$$

Here $_{13}\mathrm{Al}^{27}$ means the aluminum nucleus of nuclear mass 27 and atomic number 13; $n$ means neutron, $\alpha$ alpha particle $= {_4}\mathrm{He}^2$; the proton is written as $p = {_1}\mathrm{H}^1$.

If we represent stable nuclei in a diagram in which we have put the number of neutrons as abscissa and the number of protons as ordinates,

one finds that the stable nuclei cluster on a « line ». There are many interesting regularities fig. 6, in the location of stable nuclei in this diagram but it is impossible to go into details now. I only want to point out that nuclei with excess of neutrons have a tendency to return to the Stable configuration by emission of electrons while those which have an excess of protons emit positrons. It is clear that by neutron bombardment one tends to obtain nuclei with neutron excess while by bombardment with nuclei that contain equal number of neutrons and protons one tends to obtain nuclei which have an excess of protons. This is because the stability curve has a slope lower than 45° in the region of the heavy nuclei.

The first of the artificial elements, $Z = 43$, technetium, was discovered by C. Perrier (a native of Turin) and myself in 1937 in Palermo in material which I had obtained the previous year in Berkeley. The name commemorates the fact that it is the first artificial element. It is a homolog of manganese and rhenium. Today one has or one could have large quantities of it because it is one of the most abundant products of uranium fission. Its isotope of mass 99 has a half life of approximately 200,000 years and thus can be easily accumulated. Technetium is even practically interesting. It has a high transition temperature for superconductivity and for this reason it has been used as a coating in modern prototypes of accelerators. One of its isotopes is important in medical diagnostic, and some stars show it prominently in their spectrum (fig. 7).

The next missing element, atomic number 61, was discovered during the war by Coryell, Marinsky, Glendenning and others and it has been called prometheum because it was formed in the fire of the atomic pile. The next missing element, 85, is a higher homologue of iodine and was found by Corson, MacKenzie and Segrè in 1940. It is the last of the halogens. It does not have any isotopes of long life and sometimes it is used in biology because it likes to go to the thyroid. Francium is a homolog of cesium and it has been found among the natural radioactive substances as a rare branching. It had escaped up to 1939 when Miss Perey found it. Thus the periodic system was completed up to uranium $Z = 92$.

Is $Z = 92$ a limit, a sort of Hercules columns? Is it possible to go beyond? In 1934 Fermi, and our group in Rome bombarding uranium with neutrons observed some radioactivities which, after having ruled out that they may be due to any element heavier than lead, were ascribed to element 93. These investigations were pursued by our group in Rome, by Hahn and Meitner in Berlin and Curie and Joliot in Paris. For several years the results were hard to interpret until Hahn and Strassmann with the discovery of fission in 1938 illuminated the problem. Immediately afterwards McMillan showed that among the products of the uranium bombardment, some did not seem to be a fission fragment because they

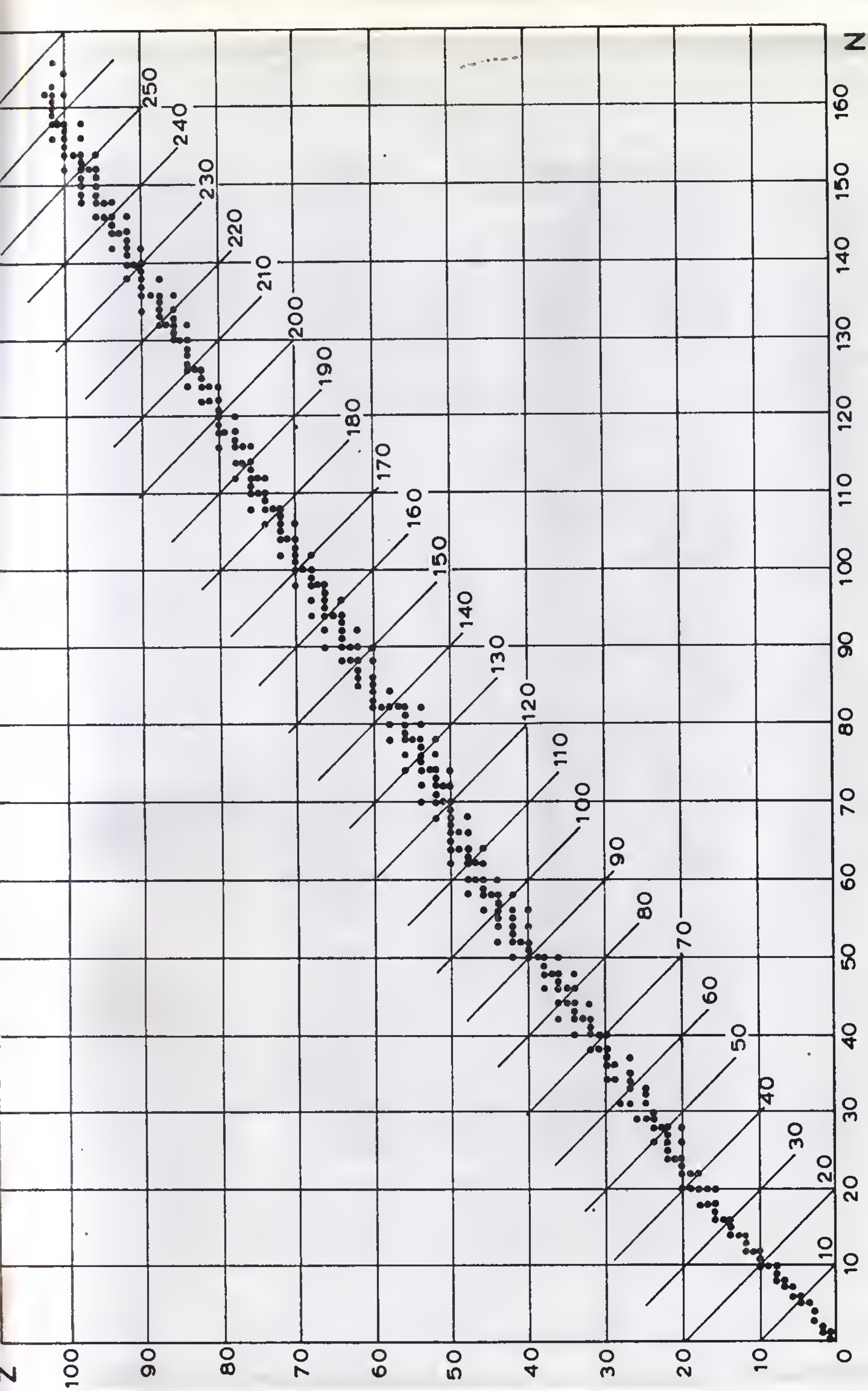


Fig. 6.

A diagram giving $Z$ and the number of neutrons contained in beta-stable nuclei.

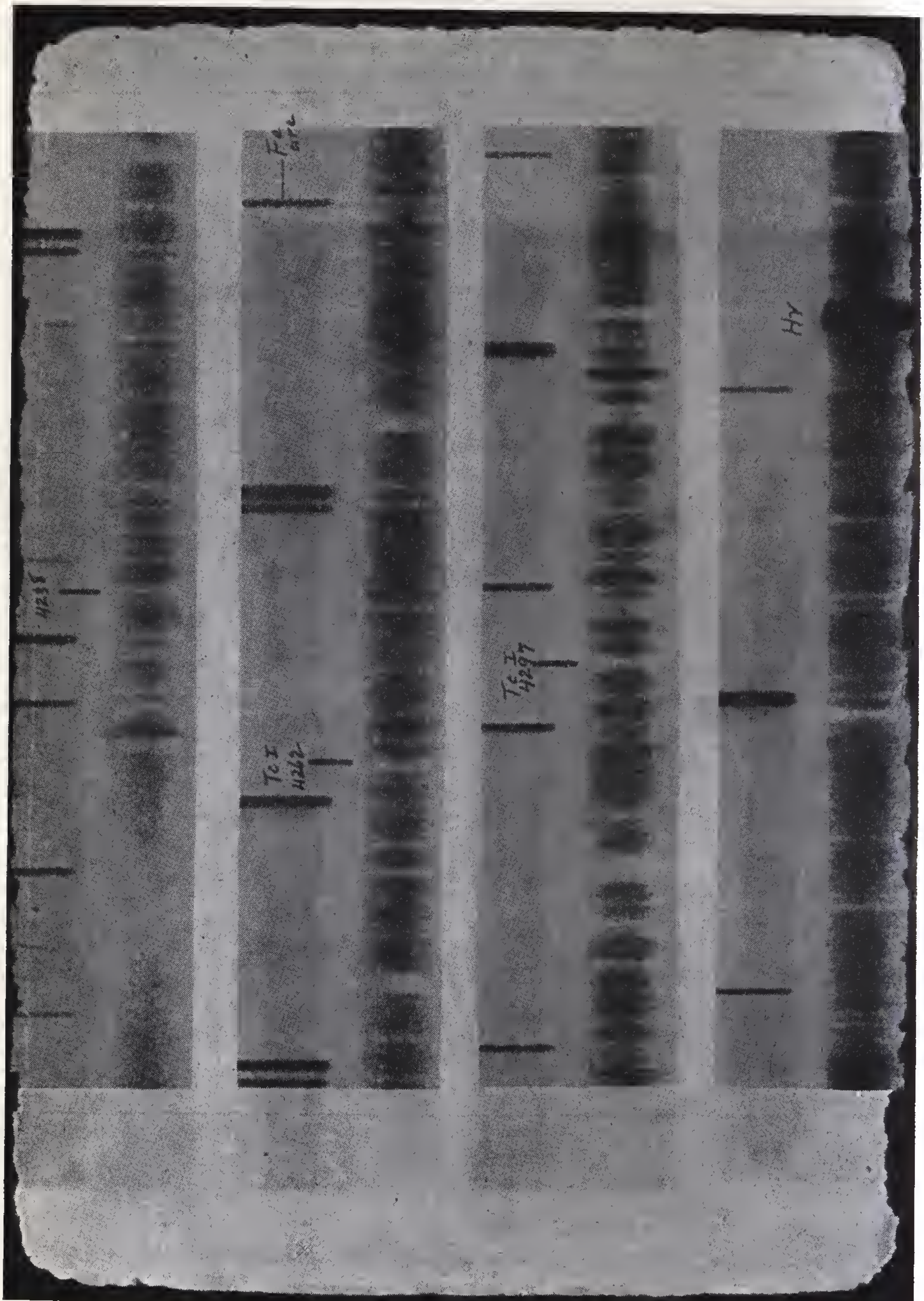


Fig. 7.

did not recoil out of a thin layer of uranium oxide. One was $U^{239}$, anothe, body of two days half-life I showed had properties very similar to those of a rare earth. It was left to McMillan and Abelson to identify it with element 93, neptunium, and to establish that it had various oxidation states, the key to its chemical separation and properties. They are thus rightly recognized as the discoverers of the first transuranium element. This work occurred in 1939-1940. We were at the beginning of the world war and nuclear physics was about to acquire an extraordinary

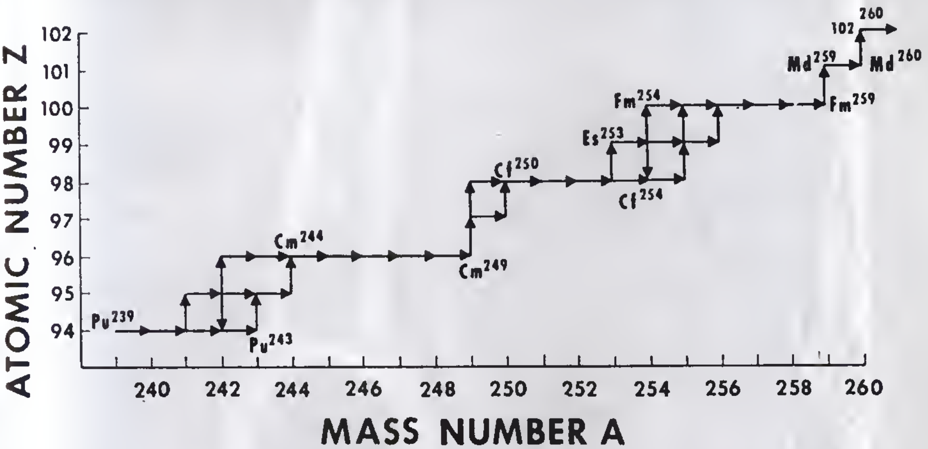


Fig. 8.

Stepwise addition of slow neutrons to $Pu^{239}$, interspersed with beta decays. The addition of a neutron leaves Z constant and increases A by one. Beta decay increases Z by one and leaves A constant.

importance in the minds of several scientists as a discipline that might give a decisive weapon. In particular one had to find nuclei other than $U^{235}$ which would undergo fission when bombarded by slow neutrons; they would open the way to the making of a chain reaction and thus to both atomic power and atomic weapons. It thus became imperative to study in detail element 94 because there were reasons to believe that the isotope $94^{239}$ could be long lived and fissionable by slow neutrons. At the beginning of 1941, Kennedy, Seaborg, Wahl, and I discovered it and showed that it could be used in reactors and in bombs. I will not go into the war work except to remind you of the discovery of spontaneous fission made independently in Russia by Flerov and Petrjak and in the United States by others. This spontaneous fission is a new decay mode to be added to the usual alpha or beta decay and for heavy nuclei spontaneous fission may become of overwhelming importance.

After the war a strong group at Berkeley comprising Seaborg, Ghiorso, and many others has devoted the last 25 years to an extensive study of

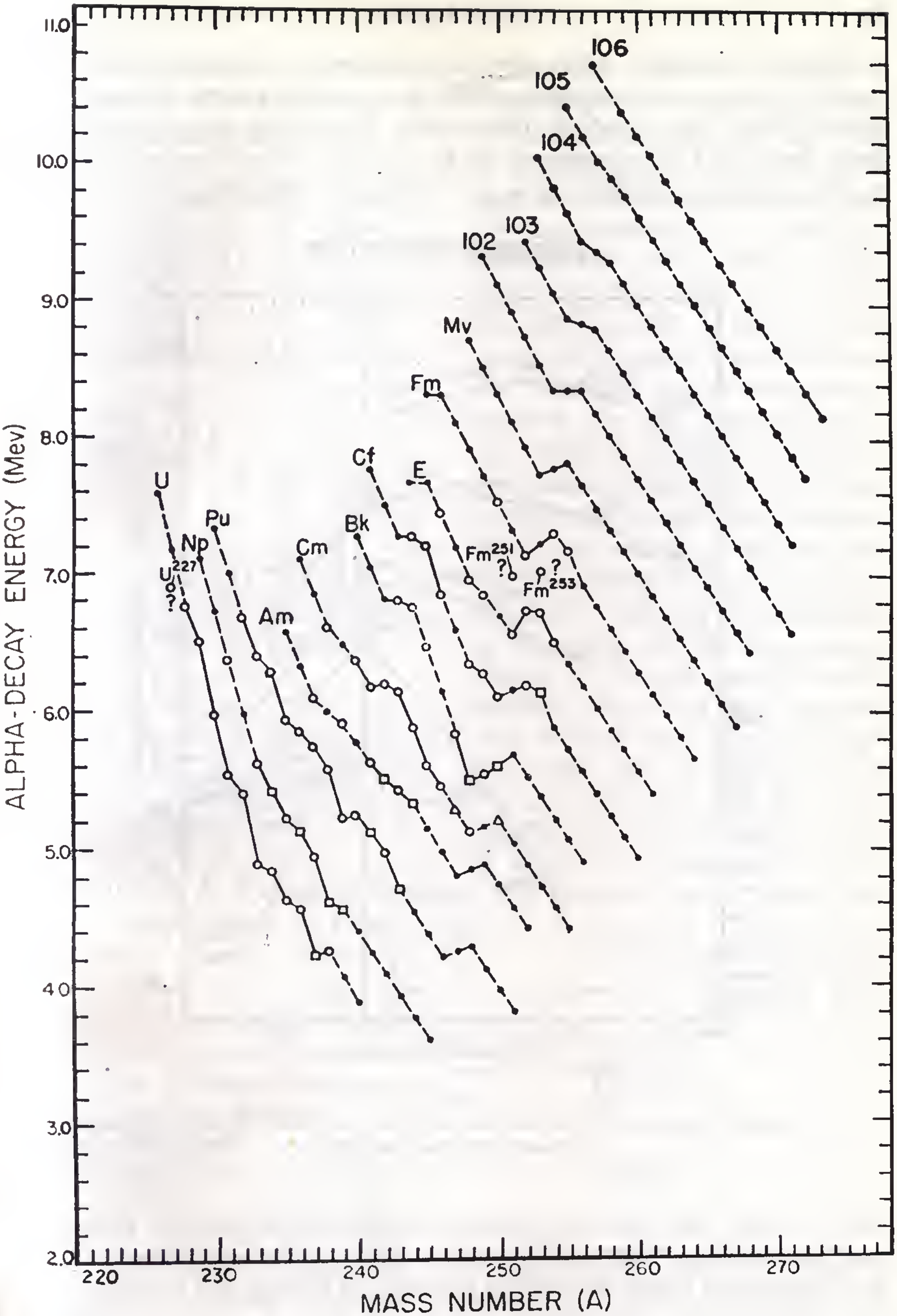


Fig. ro.

Energy released in alpha decay. The half life decreases very roughly exponentially as the energy released increases.

transuranic elements. There are two main ways to prepare transuranic nuclei. One may add neutrons either in a nuclear reactor or even in an atomic bomb (fig. 8 and 9). The nucleus with excess neutrons undergoes beta decay and thus increases its Z. By this method one may prepare nuclei above the stability curve. In a different method one may bombard

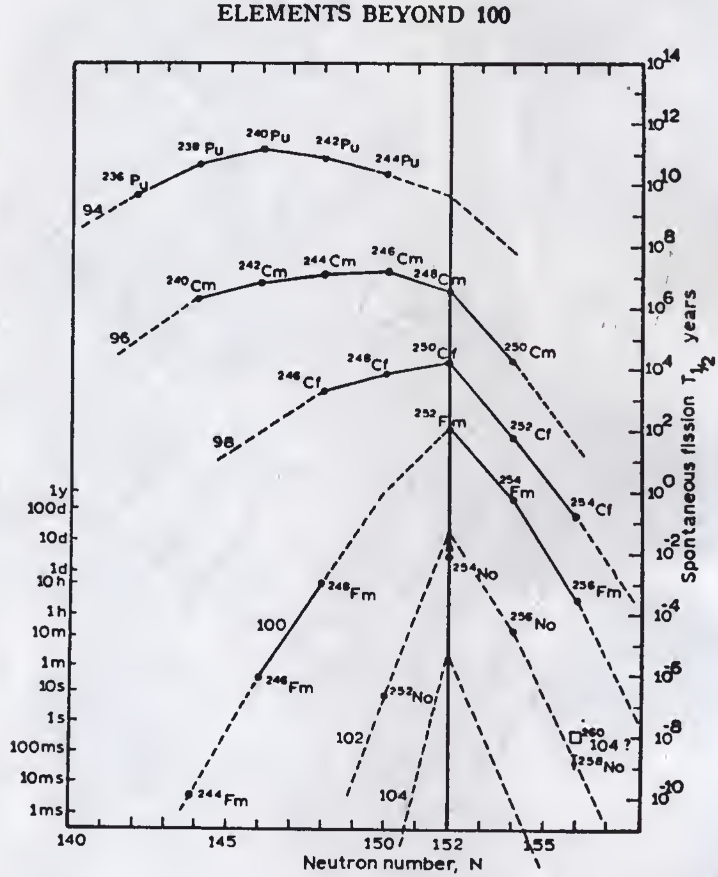


Fig. 11.

Plot of partial spontaneous fission half-life versus neutron number for even-even nuclides. (Ghiorso and Silkkeland 1967).

heavy nuclei with charged particles accelerated artificially; projectiles used are relatively light nuclei such as carbon, neon, and others. In this way one obtains nuclei which have an excess of protons and are thus below the stability curve. The limit to these operations is given by the half-life of the products and this half-life generally decreases with increasing Z. It is possible to predict the half-lifes of the nuclei formed by using interpo-

lation procedures which are based on valid theoretical ideas. Thus the data acquired from other nuclei can often be used to predict nuclear properties of a still unknown isotope. One has thus built tables and curves which allow to make valid prediction and plan experiments (fig. 10 and 11). Qualitatively alpha decay is dominated by the energy with which the alpha particle is emitted, beta decay by the energy available for the decay and spontaneous fission by $Z^2/A$. For the identification of the products one has several criteria. First of all, if it is possible to accumulate a sufficient quantity of the new substance, one may obtain the atomic number from the chemical properties. In particular in the region of the transuranics, similar to the rare earths, mainly between element 94 and 100, elution methods are most powerful and have been developed into a fine art, (fig. 12). One has thus been able to trace the filling of the 5f orbits (14 homologues of the rare earths up to $Z = 103$). The range and the mean life of alpha activities allow sometimes to decide the isotopes present. The isotopic assignement can also be obtained by cross bombardments in which one isotope is obtained by several different bombardments. It is also possible to investigate the decay products of a given nucleus and to land into some recognizable one from which one climbs back to the original mother substance. Without going into technical details it is apparent that the investigation becomes more difficult as one increases in atomic number. First the substances from which one starts become themselves more difficult to pre-

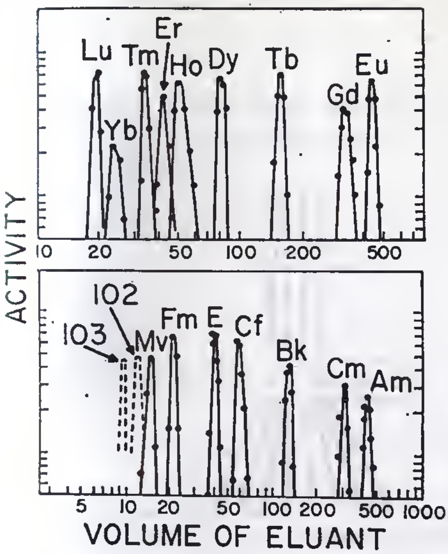


Fig. 12.

The evolution of tripositive actinide and lanthanide ions. Dowex-50 ion-exchange resin was used with ammonium alpha hydroxyisobutyrate as the eluant. The positions predicted for elements 102 and 103 are indicated by broken lines. (Seaborg 1957).

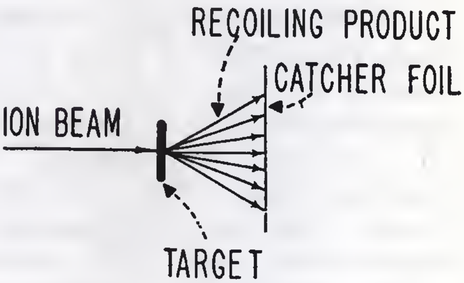


Fig. 13.

The ion beam propels the atoms that are hit on the movable catcher foil. The atoms formed are detected at a distance from the beam.

pare and all intermediate products become less stable. At the end one arrives at a situation in which one observes one atom at a time. It is thus hardly possible to seriously speak of chemical properties and the investigation becomes very slow. How one can see an atom at a time is shown by, fig. 13 and 14.

With all these resources one has arrived to Z = 104. We are thus outside of the actinide group because the new substances, 104, 105 should

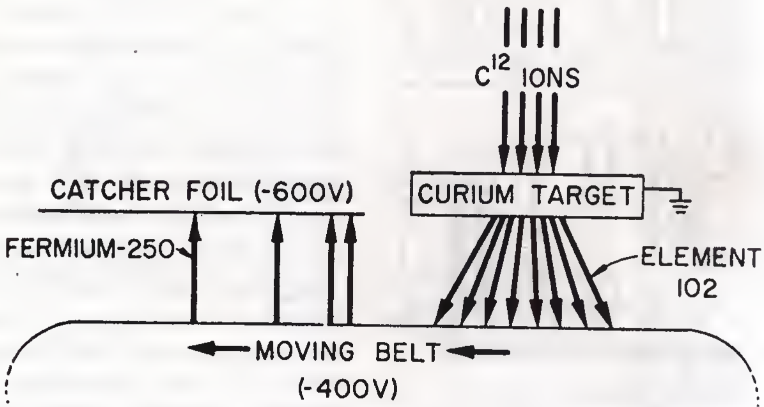


Fig. 14.

A more elaborate system for counting single atoms and their decay products. The method was used for the discovery of element 102, nobelium.

be Eka Hf and Eka Ta. However, these elements are still under very active study and one cannot say that the results thus far acquired are entirely clear.

Is this the final limit? Probably not, although the next step is going to be very difficult. If we go back to fig. 6, one may plot on a downward *z* axis the energy of the nucleus and represent according to Swiatecki the zones of stability as a long peninsula an a small island in a sea of instability, (fig. 15). On the peninsula there are some small mountain chains which correspond to the magic numbers of the shell model. At the end of the peninsula there is a channel and then a new island around Z = 114. The reason is that Z = 114 is a new magic number according to a refined shell model and also the number of neutrons, 184, seems to be magic. The arguments which lead to this conclusion are not as simple as those which lead to the classical magic numbers 2, 8, 20, 28, 50, 82, and 126. In fact they are uncertain on many accounts. They include empirical material which has accumulated and they contain extrapolations from the behavior of other nuclei. Be this as it may, it is possible that there is a region of stability around

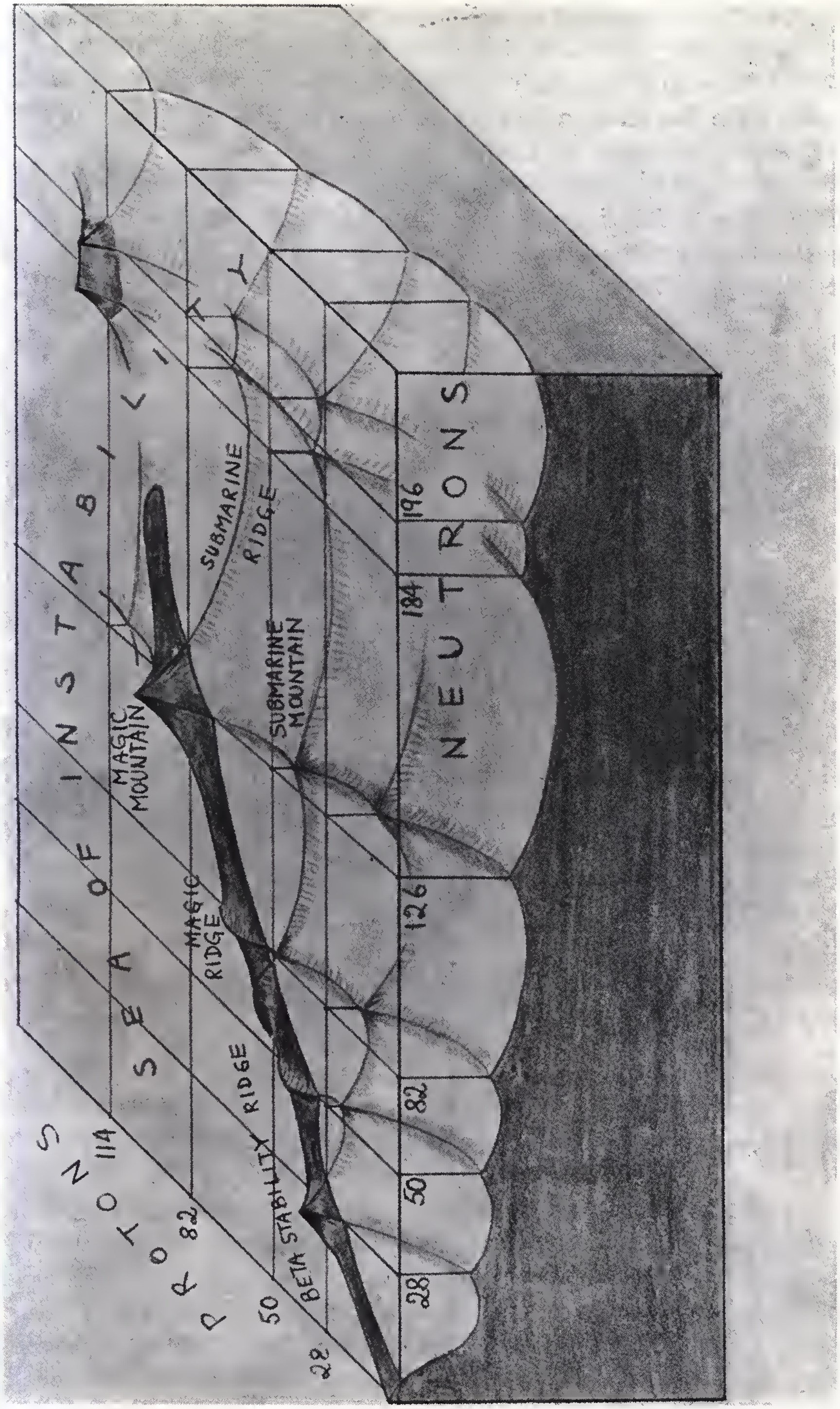


Fig. 15.

Nuclear stability regions according to Swiatecki.

$Z = 114$. This region can be reached only by parachuting on it or speaking less figuratively, one has to introduce in a target nucleus all the nucleons at once because if one were to proceed step-wise, the intermediate states would have too short a half-life to await for the next projectile. There are several proposals on how to do this.

The reactions listed below in order of increasing complexity or difficulty give a fair idea of what can be done. Reactions 1-4 use well known ions, but the targets are somewhat exotic. Reactions 5-7 require acceleration of heavy ions, beyond what has been done thus far.

(1) $$_{96}Cm^{244} + {}_{6}C^{13} \rightarrow {}_{102}No^{253} + 4n$$

(2) $$_{94}Pu^{241} + {}_{8}O^{16} \rightarrow {}_{102}No^{253} + 4n$$

(3) $$_{96}Cm^{246} + {}_{6}C^{12} \rightarrow {}_{102}No^{254} + 4n$$

(3) $$_{102}No^{254} \xrightarrow[3\text{ secs}]{\alpha} {}_{100}Fm^{250} \xrightarrow[30\text{ min}]{\alpha}$$

(4) $$_{99}Es^{253} + {}_{2}He^{4} \rightarrow {}_{101}Md^{256} + n$$

(5) $$_{98}Cf^{249} + {}_{7}N^{15} \rightarrow 105^{260} + 4n$$

(5) $$_{95}Am^{243} + {}_{10}Ne^{22} \rightarrow 105^{260} + 5n$$

(6) $$_{95}Am^{243} + {}_{7}N^{15} \rightarrow {}_{102}No^{254} + 4n$$

(6) $$_{92}U^{238} + {}^{10}Ne^{22} \rightarrow {}_{102}No^{254} + 6n$$

(6) $$_{102}No^{254} \xrightarrow[20\text{-}50\text{ secs}]{\alpha} {}_{100}Fm^{250} \xrightarrow[30\text{ mins}]{\alpha}$$

(7) $$_{90}Th^{232} + {}_{36}Kr^{82} \rightarrow 126^{310} + 4n$$

(7) $$_{72}Hf^{180} + {}_{54}Xe^{132} \rightarrow 126^{310} + 2n$$

(7) $$_{64}Gd^{156} + {}_{62}Sm^{154} \rightarrow 126^{310}$$

(8) $$_{52}Te^{130} + {}_{54}Xe^{136} \rightarrow 106^{266}$$

(9) $$_{92}U^{238} + {}_{92}U^{238} \rightarrow [184]^{476} \rightarrow 114^{298} + {}_{70}Yb^{166} + 12n$$

The expected properties of the stability zone are illustrated in fig. 16 and 17 which refers to $Z = 114$ and to the number of neutrons of 184 respectively. Please note that elements 113 to 117 are respectively analogues of thallium, lead, bismuth, polonium and astatine and thus they would have considerable chemical variety. Many attempts have been made to prepare some of the super-heavy elements; thus far none has

been successful or at least nobody has proved unequivocally that one has formed atoms with atomic numbers in the region 114. Beyond that there are even more speculative elements but I will not describe this farther horizon.

The ways of reaching the stability islands are as usual bombardments of very heavy targets with heavy nucleons or even perhaps the head on

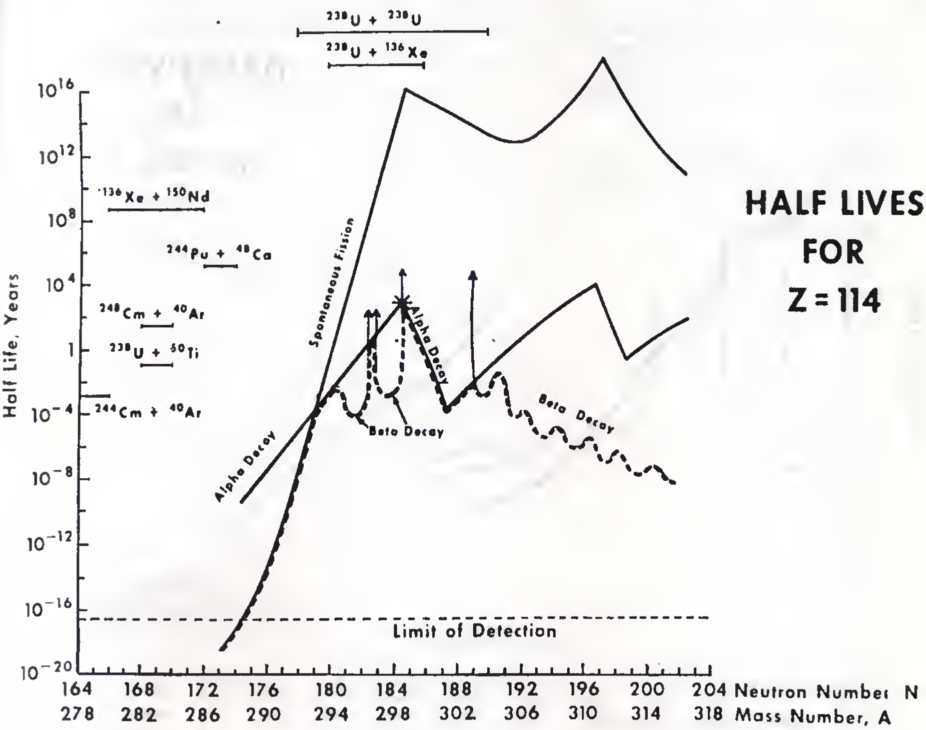


Fig. 16.

Predicted behavior of nuclei with Z = 114. The different decay probabilities for $\alpha$, $\beta$ and spontaneous fission indicate that neutron numbers 182 or 186 are the most stable.
(After Seaborg and Bloom).

collision of two such nuclei as uranium. In order to achieve these possibilities one has to wait for special accelerators and several are under construction in the United States and in Russia.

I will briefly touch now on an extension of the periodic system which could not even have been dreamed of by Mendeleev. Namely to negative atomic numbers. This perhaps may look like a joke, but what I intend by it is the preparation of nuclei and atoms of antimatter. Antiproton and antineutron have been prepared several years ago in Berkeley and in *principle* there shouldn't be much difficulty in preparing other nuclei

of antimatter. If one can endow them with positrons, one would have complete anti-atoms. Thus far the only composite nucleus of antimatter which has been prepared is the anti-deuteron and one has not even been able to attach a positron to it. Of course, it is not impossible that in some remote region of space there might be worlds of antimatter and then the anti-chemists would be there making their anti-chemistry. This anti-

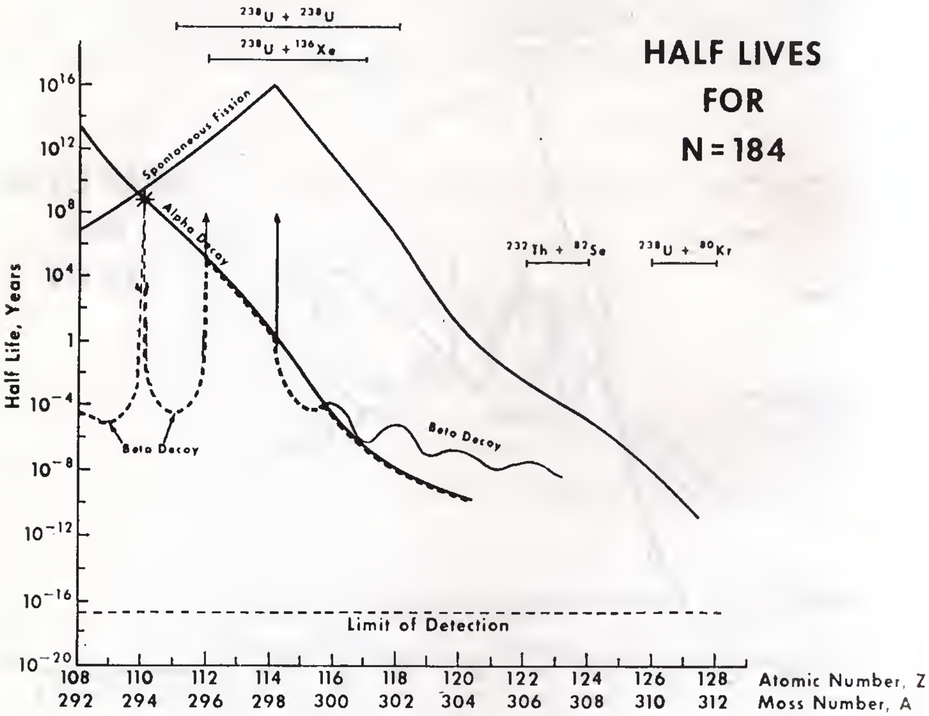


Fig. 17.

Same type of diagram for N = 184.
(After Seaborg and Bloom).

chemistry would not be particularly interesting because it would be identical to the chemistry that we do here.

As last item, I want to mention other possibilities. The replacement in the nuclei of the neutrons through lambda particles. One obtains thus so-called hypernuclei. These are well-known in several instances, but they last about $10^{-10}$ seconds. Although they are not useful subjects for the study of chemical elements, nevertheless, they have interesting properties from the point of view of nuclear physics. It is also possible to replace not the constituents of the nucleus but the electrons of the atom

or part of the electrons of the atom by heavier particles. In this way one has the mu-mesic, pi-mesic, and recently K-mesic atoms. These are atoms in which one electron has been replaced by a muon, pion, or a kaon. It won't be long before one will replace also one of the electrons by an anti-proton. These atoms are especially interesting from the point of view of nuclear and atomic physics. They represent typical extensions of the old Bohr hydrogen atom. Their study by now is quite advanced and has given many information on nuclear dimensions, nuclear structure, masses of elementary particles, spin and magnetic moment of the same. They even present problems at the borderline between chemistry and solid state physics.

Thus in 100 years we have travelled a long way from Mendeleev. Who knows in 100 more years what our children might have reached?

G. N. FLEROV and S. A. KARAMIAN (*)

# The Search for Superheavy Elements in Nature: Foundations and Prospects.

## 1. Introduction.

A hundred years ago Dimitri Ivanovitch Mendeleev discovered the law of periodicity in the variation of the properties of the elements as a function of the atomic number, that was of great importance in the development of the physical and chemical sciences. During the life of D. I Mendeleev the heaviest known element was uranium — the element with atomic number 92. Mendeleev wrote seventy years ago in « Foundations of Chemistry »: Being convinced that uranium research, to begin with on its natural sources, shall lead to many new discoveries yet, I boldly recommend to those who are looking for new research subjects to work with special care on uranium compounds [1]. Indeed, the study of uranium lead to the discovery of natural radioactivity, an event that marked the beginning of the whole modern nuclear physics. By studying nuclei the characteristic laws of the periodical variation of properties due to the filling up of nuclear shells were discovered.

The principal role played by the atomic weight of the isotopes, which determines together with the atomic number of the element all the nuclear properties of each isotope among others its stability, became clear. One of the most interesting physical phenomena — the existence of an island of nuclear stability in the region $Z > 90$ (Th, U, ...) can be explained at present with the appearance of shell effects in the structure of nuclear matter.

Studying the natural radioactivity of thorium and of the uranium isotopes through the efforts of Marie and Pierre Curie and of other investigators of the first half of the 20th century it was possible to obtain information on the short lived elements with $83 < Z < 90$, that are found

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in radioactive equilibrium with their long lived ancestors in its decay products. The elements of francium and astat, it is true, were synthesized artificially before they were found in the decay products of thorium and uranium. The element with $Z = 61$ — promethium — which does not exist in nature, was first discovered in the products of the neutron induced fission of uranium nuclei.

The presence in natural earth minerals of the three long lived nuclei $^{232}$Th, $^{235}$U, $^{238}$U, allowed as a result of the nuclear physics progress to synthesize artificially a large number of isotopes of the 13 new elements with atomic number from $Z = 93$ to $Z = 105$ and to study their properties.

The first attempt to obtain new transuranic elements was undertaken by Enrico Fermi in his experiments of thirty five years ago investigating the interaction of neutrons with matter. And though this attempt failed, afterwards the successful synthesis of elements beginning from Np and Pu up to Fm was achieved precisely with Fermi's method, but using considerably higher neutron densities. A systematic program of synthesis of new elements using neutron irradiation was carried out in the USA after the war under G. Seaborg's direction.

Nine new elements were investigated with a high degree of reliability and their physical and chemical properties were studied. However, this method apparently exhausted itself since even using the underground atomic explosions, which release extremely high density of neutron fluxes, does not permit to make progress in the synthesis of elements beyond the 100th element (Fm). This stage of the work on the synthesis of the transuranic elements is described in detail in Seaborg's review article [2].

Up to the present time the study of heavy nuclei continues to be one of the most interesting branches of nuclear physics. The influence of this scientific-technical trend on many aspects of people's practical activity is enormous. The nuclear physics of fissionable elements gave to mankind giant new technological possibilities, on whose basis the world's most advanced countries developed a powerful industry and energetics.

At the same time in the field of the chemical sciences the study of elements at the border of Mendeleev's periodic table didn't lead to such revolutionary discoveries, which possibly was what Dimitri Ivanovitch Mendeleev hoped for.

It turned out that the elements with $89 < Z < 103$ have very similar chemical properties and form the group of actinides, similarly to the earlier known group of lanthanum analogs, the lanthanides. The investigation of the actinides chemical properties revealed itself as one of the most interesting problems of present-day's chemistry, having a most

important practical significance in connection with the development of nuclear energetics.

New materials and compounds of artificially synthetized transuranic elements were made, which at present are used intensively in nuclear industry and technique. However, because of the actinides' chemical similarity, the materials and chemical compounds of each of them do not possess essentially original mechanical, optical and electrical properties. Qualitatively new chemical properties are present only in elements with $Z > 103$, the first of which — kurchatovium, discovered in 1964 at Dubna — has a lifetime of tenths of a second.

It should be remarked here that the problem of synthesis of the elements with $Z > 101$ possesses definite specific characteristics and fundamental difficulties. The short lifetime of the isotopes of these elements, of the order of seconds and fractions of a second, does not permit one to identify these elements by means of ordinary chemical methods in experiments on their synthesis. The low production cross-section of elements with $Z > 101$ in reactions with accelerated heavy ions leads to an insufficient statistical reliability of the experiments and puts at the limit of possibilities the experiments on the synthesis of elements 104 and 105.

In spite of these difficulties, we were able in Dubna for the first time to synthesize and unambiguously to identify six isotopes of element 102 [3], three isotopes of element 103 (see the review [4]), the element 104 [5], [6], and to obtain preliminary data on the properties of element 105 [7] (1).

Extremely important experiments on the chemistry of elements 102, 103 and 104 were carried out with the unique method of gas chromatography of chlorides [8], [9], [10]. The fundamental character of the results of these works consists in the experimental determination of the limit of the actinide group of elements. In spite of the success of these experiments, it should be remembered that in this case the chemical experiments were carried out for an emitter with already known decay properties, while for the elements with $Z < 101$ the picture was inverted: the chemical separation of the element preceded the investigation of its decay characteristics. This circumstance reflects one of the development trends of the work on the synthesis of the transfermic elements, consisting in the fact that as we go to heavier elements the problem of studying their properties becomes to a smaller degree a chemical problem and to a higher degree reduces to an investigation of the decay properties of the short

(1) Most recently new reliable results have been obtained in Dubna on the spontaneous fission of element 105 [49], [50], [51].

lived nuclei with definite $Z$ and $A$. Most probably, the detailed investigation of the chemical properties of the elements near the border of the actinide's group ($Z = 102$-$105$) will turn out to be impossible to carry out. The practical application of these elements is, apparently, also impossible due to their short lifetime and to the lack of a method that permits to obtain these elements at least in microweight quantity.

Here, clearly, we entered such a region, in which nature strongly opposes our attempts to penetrate her misteries. Therefore, on one hand, new results are obtained at the price of very large efforts, on the other, these results do not have practical application. At the same time if the more distant transuranic elements are relatively long lived, then their study has an enormous scientific and practical significance. Therefore, it is not surprising, that the question on the possible existence of a new island of nuclear stability attracts at present the interest of a large number of specialists in the whole world.

## 2. The physical foundations of the hypothesis on the existence of stable superheavy elements.

If one remembers the periodicity in the variation of nuclear properties as the number of protons ($Z$) and neutrons ($N$) in nuclei changes, then it does not seem senseless to ask the question about the existence of a new island of nuclear stability in the region of high values of $Z$ and $N$. It is possible to express qualitative considerations on the fact that as the number of protons and neutrons grows, the role of shell effects in nuclei, generally speaking, may weaken as a result of the increase of the density of single particle states near the Fermi surface. Besides, an increase in the proton number in nuclei with $Z > 100$ must lead to a catastrofic weakening of the stability of nuclei with respect to spontaneous fission and $\alpha$ -decay due to the increase of the Coulomb repulsion forces in nuclei. However, these qualitative considerations do not help to clarify the question of the stability of the heavy magic nuclei and it is necessary to have a quantitative investigation of this problem. Such an analysis was carried out in the last few years by the theoreticians of several countries and gave hopeful results. The early works [11], [12], [13] were dedicated to the determination of new proton and neutron magic numbers. Later it became clear that the knowledge of these numbers is absolutely insufficient for the solution of the question of stability numbers with one or another number of nucleons. It was necessary to evaluate the mass of the nuclei and its deformation energy. The first calculation of nucleon masses in the hypothetical region until $Z = 140$ and $N = 210$

were done by Myers and Swiatecki [14]. Already from these data it was possible to obtain some conclusions on the higher stability of nuclei with $N = 184$ and $Z$ near 126. However the exact calculation of the fission barrier of the heavy nuclei became possible only after Strutinsky developed the method of calculating the shell correction [15], [16], for the evaluation of the potential energy of nuclei as a function of their deformation. With the help of this method in the papers [17], [18], [19], [20] the fission barriers and masses of the nuclides of transuranic elements were calculated in a wide interval of variation of $Z$ and $N$ using different sets of parameters, essential for the calculation.

The calculated mass values of nuclei permit one to determinate the energy of $\alpha$ -decay and with the help of phenomenological formulae, the half-lives of $\alpha$ -decay for these nuclei [20]. On the basis of the calculated fission barriers it was possible also to estimate the spontaneous fission half-lives of superheavy nuclei.

Similar calculations were carried out in the USA by an international group of physicists [21], [22], [23]. At present with the development of the theory there are increasing possibilities of evaluation of the potential energy of nuclei as a function of different types of deformation for a wide range of values of the parameters of deformation up to very high values [24]-[26].

All the calculations which are available at present, without exceptions, give essentially one and the same result, independently from the choice of parameters of calculation: they predict the existence of islands of increased stability of nuclides heavier than all those known at this time.

The different calculations give, however, essential differences in the determination of the limit of the region of stability and its center of mass. The absolute precision of the lifetime of nuclei from the new region of stability is not sufficient, there being a possibility of errors of a hundred thousand times. A qualitative improvement of the theory trying to make it more precise is at present apparently impossible. Summarizing, one should remark, that the theory at present is not able to give a precise answer to the question of which isotope should be the most stable and what will be its lifetime. Those, who try to extract such an information, are performing an unlawful operation. The fundamental prediction of the theory on the existence of a new island of stability of nuclei with possibly very large lifetimes is a significant success of the theory, but to her qualitative results one should not attach an absolute significance.

Only experimental investigations allow one to obtain a reliable quantitative information on the stability of superheavy elements. As men-

tioned before, the theory does not forbid the possibility of a very high lifetime for these elements, comparable even to the age of the sun's system.

It there exists some isotope of a superheavy element with a lifetime $> 10^8$ years, then it must be conserved in the earth up to this time, at least in very small quantities. If the lifetime of the nuclide is contained

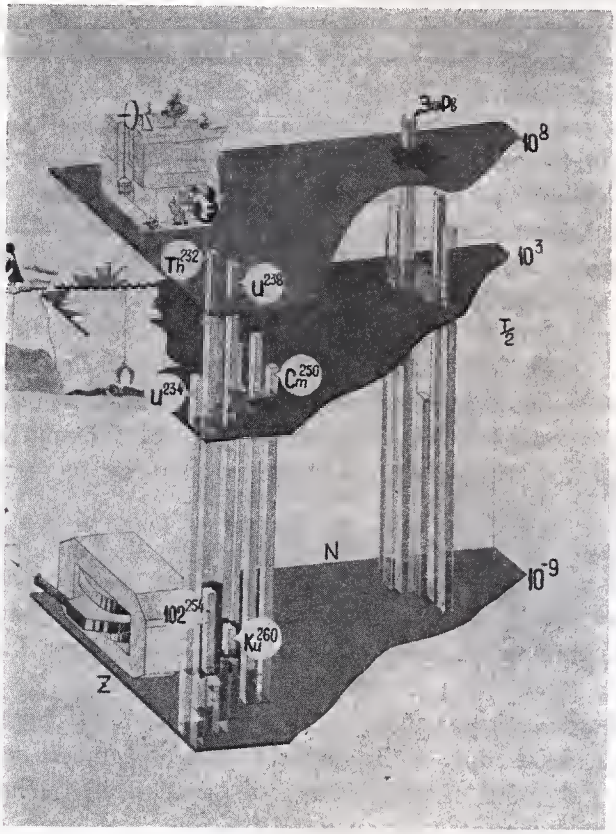


Fig. 1.

Schematic representation of the different ways of obtaining the isotopes of superheavy elements with different $Z$ and $N$ values depending on their lifetimes.

in the interval $10^5 < \tau_{1/2} < 10^8$ years, then the nuclei of this nuclide may enter in the composition of cosmic rays, since the active zones of the Universe are placed at distances from the solar system $> 10^5$ light years. In this case one can look for very small quantities of this element also on the earth, due to the constant arrival of these nuclei from the cosmos, compensating their radioactive decay. There should establish itself a definite equilibrium of arrival and decay of the given nuclide. And finally

if the lifetime is less than $10^5$ years we can count only on the artificial synthesis of the new element in laboratory conditions. These considerations are illustrated in fig. 1.

In the above mentioned considerations we tacitly assumed that the nuclei from the new region of stability may be generated in the process of a star synthesis of nuclei. According to present-day representations the transuranic elements are synthesized as a result of fast successive capture of neutrons by the nuclei of light elements in the explosions of supernovae (the so-called r-process). In an r-process is it possible to produce nuclei with $A > 280$? In our opinion it is at present difficult to give a definite answer to this question. The evaluation of an r-process necessitates the knowledge of the binding energies of the neutron, the fission barriers and the periods of spontaneous fission for nuclei that possess a very high excess of neutrons for $Z > 92$. We don't have exact information of this type at the moment, and even more, a series of physicists (among whom the author [27]), manifest the idea that in general our representations about nuclear stability of neutron enriched nuclides are not correct and that the neutron binding energy becomes zero only for nuclei with a much larger excess of neutrons than follows from the semiempirical formulae for the nuclei's mass. However, as an example, one may say, that in the papers [28], [29] a calculation was done on the r-process with a definite hypothesis about the properties of heavy nuclei and the result obtained, was that the r-process is cut off in the region $A = 270$-$275$ due to the large probability of induced fission in nuclei in this mass region. There are also more optimistic calculation result [30]. Probably, there is no reason to believe, that any result of these calculations is final. Besides, even if an r-process does not lead to the formation of superheavy nuclei, there may exist apparently some other ways for their synthesis in stars. One of the interesting possibilities of synthesis of superheavy elements in pulsars are being considered at present by italian physicists [31]. One should not, however, forget that the amount and distribution in the Universe of these nuclei depend in an essential way from the type and details of the process responsible for its formation.

## 3. Attempts at the experimental discovery of superheavy elements.

Concerning the history of this question it is necessary to remark that already in the early work on the natural radioactivity of natural materials some facts were observed which up to the present are not satisfactorily explained. Prof. Schintelmeister during a long time studied the natural $\alpha$ -emitters [32] and observed anomalous energies of $\alpha$ -par-

ticles and also unusual chemical properties of these emitters (in some cases similar to the properties of Osmium), but he could not identify exatcly these radioactivities. Recently we learned that Irene Curie in the last years of her life also worked on « strange » $\alpha$ -radioactivities which were difficult to connect with known natural $\alpha$ -emitters. Similar results were obtained in the experiments of dr. Gentry, who studied the pleocroistic rings in natural mica arising around the inclusions of $\alpha$ -radioactive elements in the targets [33]. Finally prof. Tcherdinzev for many years investigated the unusual chemical properties of a natural $\alpha$ -emitter with $E = 4.65$ Mev and concluded that this relatively rare radioactivity also shows chemical properties similar to those of Osmium [34].

If we come back to our days, then the communication by prof. Fowler of the observation of very heavy nuclei in primary cosmic rays [35] was most exciting. In these experiments large surface photoemulsions were lifted by balloons to a considerable height. Analizing the developed emulsions, separate tracks with very high density of ionization were found, which according to the authors belonged to nuclei with $Z > 100$. Later some doubts were raised on whether there was enough precision in the determinations of the $Z$ of the particle by the track density which it left in the photoemulsion. Fleitscher and Price [36] using plastic detectors to detect heavy nuclei in the composition of cosmic rays came to the conclusion that it is impossible to detect nuclei with $Z > 92$. Apparently, more experiments in this direction are necessary. If prof. Fowler's result will be confirmed, then it will mean that long lived superheavy nuclei from a new region of stability ($\tau_{1/2} > 10^5$ years) exist and that they are synthesized in the depths of the cosmos.

Deserves attention also the information available on the excess of radiogenic Xenon and its unusual isotopic composition in a series of meteorites in comparison with that quantity of Xe which should be obtained from the spontaneous fission of the $^{238}U$ contained in the meteorites [37]. These facts may be connected with the presence in the meteorites' content besides $^{238}U$ of some other spontaneous fissionable emitter, that possibly, at present has completely decayed leaving however behind an excess of Xe. Price and Fleitscher have recently completed an investigation [38] in which they measured the lenght of fission fragment tracks, detected in quartz contained in those meteorites, that showed an anomalous content of Xe. No significant difference between the lenght of these tracks and that of the tracks of fragments from induced fission of uranium nuclei and from the computed values of spontaneous fission of $^{244}Pu$ ($\tau^{\alpha}_{1/2} = 7.5 \cdot 10^7$ years, $\tau^{s.f.}_{1/2} = 2.5 \cdot 10^{10}$ years). On this basis it was deduced that the observed excess of radiogenic Xe is connected precisely with the presence of $^{244}Pu$ in the initial composition of meteorites. It seems to

us, that this conclusion does not follow necessarily from the experimental facts, since the lenght of fragment tracks of a superheavy element spontaneous fission ($Z > 100$) may also turn out to be very near that observed for the uranium fission. Here it should be recalled that the question of the mass distributions of the fragments of spontaneous fission of superheavy elements and of their energy balance in this process is completely unclear.

Lately in the USA, an attempt to discover superheavy elements in several samples containing platinum and gold was made. The choice of these elements was determined by the following reasons:

1. on the basis of experiments on kruchatovium chemistry it seems quite probable the hypothesis that elements with $105 < Z < 115$ will have chemical properties similar to the elements from Ta up to Bi;

2. the calculations of S. G. Nilson and al. [21] predict the longest lifetime for the element with $Z = 110$, which according to the first hypothesis seems similar to platinum.

Concentrating the efforts on the study of platinum containing materials a group of american scientists attempted to discover the elements 110 with the help of a wide spectrum of methods: by fragments and neutrons from spontaneous fission, by $\alpha$ and $\gamma$ -emissions of ekaplatinum nuclei. Also experiments on the X -ray fluorescence, mass spectromatric and activation analysis of platinum samples were carried out. These experiments were briefly described in the papers [39], [40]. An attempt was made to observe the thermal neutron induced fission of ekaplatinum [41]. In all these experiments a negative result was obtained; only the upper limit of the hypothetical ekaplatinum content in the samples is given ($< 10^{-10}$ gr/gr). The application of an entire series of different methods in the search for ekaplatinum makes the negative result obtained sufficiently reliable, but it seems to us that the sensitivity of the experiments can be considerably increased compared to those performed in the USA. The method for revealing superheavy elements by spontaneous fission, probably, occupies a special place. Its sensitivity is very high; the use of large proportional counters and in recent years of dielectric detectors of fission fragments gives the possibility of revealing the spontaneous fission of elements with a very long lifetime, up to ($10^{21} - 10^{22}$) years, or very small concentrations of more shortlived spontaneous by fissionable emitters. If any one of them has a lifetime relative to spontaneous fission of $10^8$ years, then it can be revealed in matter with a concentration down to $10^{-14}$ gr/gr. A great advantage of this method consists also in the limited number of background sources in experiments on spontaneous

fission; for natural materials, as background source may act only the $^{238}U$ spontaneous fission, the neutron induced fission of uranium and thorium nuclei and the fission of heavy element nuclei (Bi, Pb, ...) by cosmic rays. Besides the high sensitivity and, as a rule, the low background, this method is also good because the radioactive decay of superheavy elements in practice must inevitably terminate with spontaneous fission (either the initial longlived element or its daughter products spontaneously fission after one or several $\alpha$ -decays).

For these reasons, we in Dubna chose the method of recording the spontaneous fission of these elements as the basic way of searching for superheavy elements. Since we understood that the present theory is unable to predict exactly $Z$ of the longest lived superheavy nuclide, we did not restrict ourselves to the study of samples containing any single element. The materials containing bismuth, lead, tallium, mercury, tungsten, were checked. Besides, the samples were often of a complex chemical composition and consisted of many components. Most of all were investigated different materials containing lead. Taking into account that the chemical properties of lead are not as selective as for instance the properties of platinum, it is possible to understand the presence in the samples investigated of a great number of different micromixtures. Our first experiment [42] consisted in the following: a lead foil of $10^4$ cm$^2$ area in contact with a mylar film practically faultless, was exposed during 100 days underground at a depth of 40 m in order to protect it from cosmic rays. After analyzing the film seven tracks of fission fragments were found. Analyzing a similar film of twice the area which was not in contact with lead, only two tracks were recorded. The uranium content of the mylar and lead foil was on the level of $10^{-10}$ gr/gr and in no way could be responsible for the observed effect. The result obtained is sufficiently reliable, but the total number of recorded events is very small.

In order to increase the statistical accuracy of the experiments old (several hundred or tens years of age), glasses, mirrors, fragments of glass windows and so on, containing lead, tungsten, tallium and bismuth, were investigated. In all these cases during a long time interval were accumulated in the glass the tracks of fragments from the spontaneous fission of those emitters which were constituents of the glass or of the materials in contact with it (meaning amalgam in the case of mirrors; the lead frame in that of the glass windows and so on). In some of these samples a large number of fission fragment traces were revealed, which in no way could be explained in terms of the presence of uranium in the material investigated. The uranium content in the materials was determined with very high accuracy by irradiating the samples with slow neutrons in a reactor. Besides the uranium spontaneous fission, a possible background could

TABLE I.

*Results of the investigation about the content of an unknown spontaneously fissionable emitter on old lead glassed.*

| Number of samples | Age (years) | Number of tracks | Volume ($cm^3$) | T (years) | Number of tracks of uranium |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 1 | 12 | 1 | 0,20 | $6.10^{21}$ | — |
| 2 | 23 | 5 | 0,44 | $7.10^{20}$ | — |
| 3 | 23 | 0 | 0,22 | $3.10^{21}$ | — |
| 4 | 23 | 0 | 0,22 | $2.10^{21}$ | — |
| 5 | 180 | 10 | 0,05 | $4.10^{20}$ | 0,5 |
| 6 | 180 | 1 | 0,8 | $6.10^{22}$ | — |
| 7 | 23 | 11 | 0,44 | $7.10^{20}$ | — |
| 8 | 30 | 10 | 0,15 | $4.10^{20}$ | — |
| 9 | 5 | 0 | 0,05 | $4.10^{20}$ | — |
| 10 | 5 | 0 | 0,11 | $4.10^{20}$ | — |
| 11 | 10 | 2 | 0,16 | $9.10^{20}$ | — |
| 12 | 10 | 14 | 0,8 | $6.10^{20}$ | — |
| 13 | 10 | 1 | 0,08 | $9.10^{20}$ | — |
| 14 | 33 | 2 | 0,2 | $7.10^{21}$ | — |
| 15 | 33 | 4 | 0,4 | $7.10^{21}$ | — |
| 16 | 35 | 1 | 0,05 | $3.10^{21}$ | — |
| 17 | 22 | 3 | 0,08 | $1.10^{21}$ | — |
| 18 | 29 | 1 | 0,06 | $3.10^{21}$ | — |
| 19 | 29 | 0 | 0,1 | $4.10^{21}$ | — |
| 20 | 15 | 0 | 0,03 | $7.10^{20}$ | — |
| 21 | 20 | 0 | 0,04 | $2.10^{21}$ | — |
| 22 | 14 | 0 | 0,05 | $1.10^{21}$ | — |
| 23 | 14 | 12 | 0,61 | $2.10^{21}$ | 3 |
| 24 | 30 | 100 | 0,62 | $2,7.10^{20}$ | 2 |
| 25 | 10 | 2 | 0,12 | $2.10^{21}$ | — |
| 26 | 20 | 2 | 0,07 | $1.10^{21}$ | — |
| 27 | 20 | 3 | 0,09 | $8.10^{20}$ | — |
| 28 | 20 | 1 | 0,03 | $1.10^{21}$ | — |
| 29 | 20 | 2 | 0,06 | $1.10^{21}$ | — |
| 30 | 20 | 4 | 0,08 | $7.10^{20}$ | — |
| 31 | 15 | 0 | 0,23 | $3.10^{21}$ | — |
| 32 | 15 | 0 | 0,28 | $4.10^{21}$ | — |
| 33 | 350 | 0 | 0,01 | $1,3.10^{22}$ | — |
| 34 | 17 | 0 | 0,06 | $1.10^{21}$ | — |
| 35 | 17 | 0 | 0,03 | $2.10^{20}$ | — |
| 36 | 11 | 0 | 0,03 | $4.10^{20}$ | — |
| 37 | 14 | 0 | 0,03 | $9.10^{20}$ | — |
| 38 | 100 | 4 | 0,66 | $4.10^{21}$ | 2,4 |
| 39 | 200 | 20 | 0,13 | $1.10^{20}$ | 3 |
| 40 | 200 | 18 | 0,10 | $1,3.10^{20}$ | 4 |
| 41 | 200 | 37 | 0,15 | $1.10^{20}$ | 3 |
| 42 | 40 | 14 | 0,38 | $1,4.10^{21}$ | — |

be the lead fission by cosmic rays. At present there are no direct experimental data on the probability of lead nuclei fission by cosmic rays at sea level. However, the fact that many lead glasses do not show the effect, proves the insignificance of the background. These experiments are described in the papers [42], [43]. The results of the irradiation of lead containing samples are reported in table 1 [43]. In some samples a very high

Fig. 2.
Photograph of some of the samples of old glasses investigated.

level of the effect was revealed, for instance in one of the glasses prepared 30 years ago one hundred tracks of fission fragments were recorded with an uranium background of two tracks. In samples containing other elements (Bi, Pb, Hg, W) no large number of tracks from spontaneous fission fragments was detected, however this may be connected also with random causes since the number of samples investigated in this case was not very large. Some of the glass samples investigated are shown in fig. 2.

It is necessary to add one explanation to table 1: we do not know the half-life period of the spontaneously fissioning emitter whose fission fragments are recorded in the glasses, therefore it is impossible to calculate the concentration of this emitter in the material. In this connection the observed effect was compared to the number of lead nuclei in the

sample volume which was analyzed and the value of the apparent half-life of lead relative to spontaneous fission was calculated. This value would have a physical meaning, if the lead really underwent spontaneous

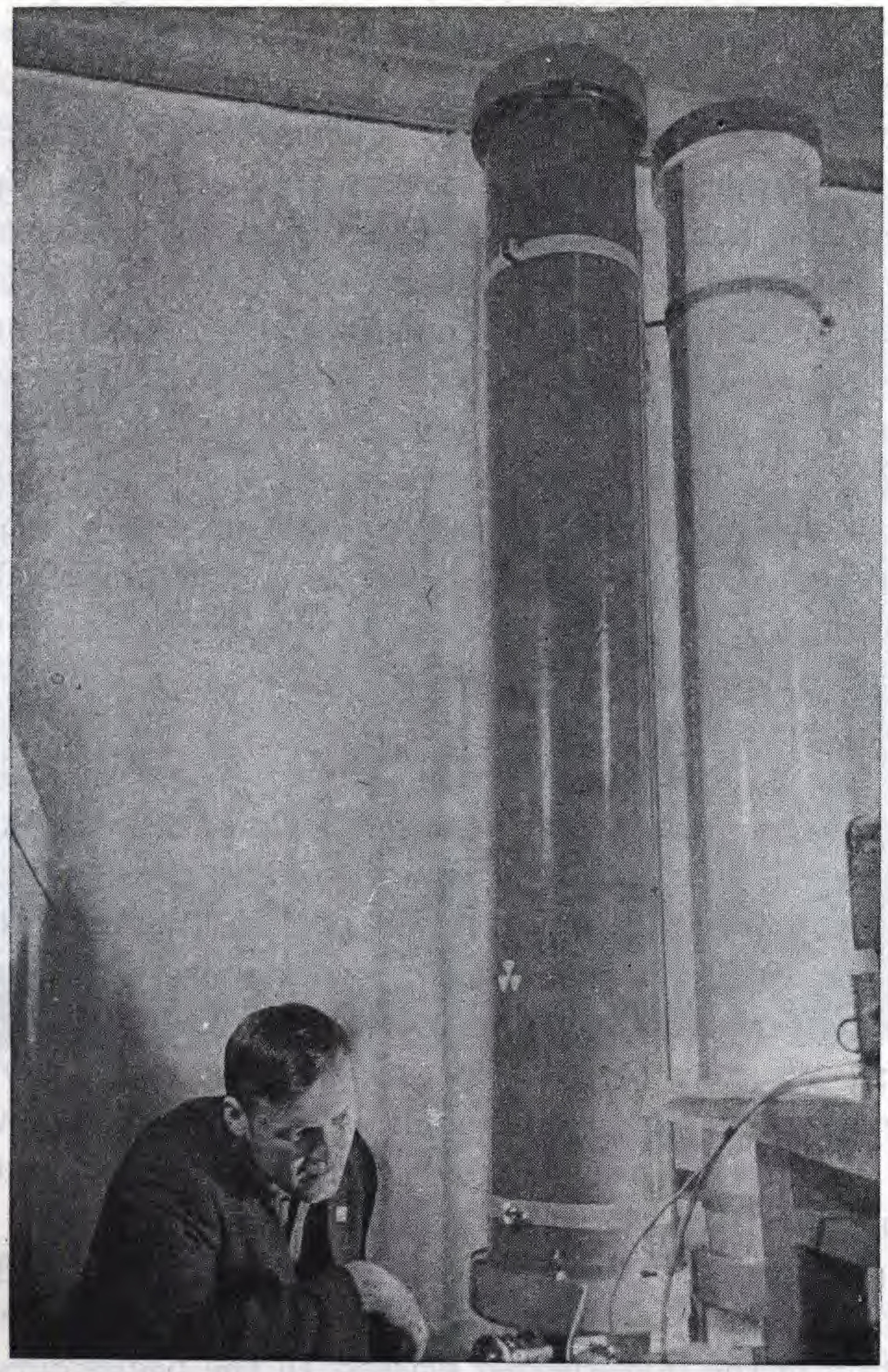

Fig. 3.
The large proportional counters used to detect the spontaneous fission fragments [44].

fission. Since this is unreal, the quoted value of the apparent half-life of lead is nothing else than $T = \frac{\tau_{1/2} n_{Pb}}{n_{\text{s.f.e.}}}$ where $\tau_{1/2}$ is the unknown half-life of spontaneously fissionable emitter, $n_{\text{s.f.e.}}$ — is the number of nuclei of this emitter in the sample, $n_{Pb}$ — is the number of Pb nuclei in the sample. I. e., $T$ is inversely proportional to the concentration of spontaneously fissionable emitter and to its rate of decay $\lambda$. If $\tau_{1/2} = 10^8$ years,

then with a minimum value $T = 10^{20}$ years the sample contains one atom of the spontaneously fissionable nucleus every $10^{12}$ atoms of lead; in samples with larger values of $T$ there are still less of these nuclei.

All glasses mentioned in table 1, contained a large quantity of lead (from 10 to 50% in weight), but by far not all of them showed the effect of spontaneous fission. Consequently, there lacks whatsoever correlation between the lead content and the spontaneously fissionable emitter content in the samples. This fact means that either the spontaneously fissionable emitter, being ekalead, is nonetheless very different from lead in its chemical properties, or the given emitter does not belong at all to the IVth group of Mendeleev periodic system and is present in the samples containing lead by chance, having as its carrier some other element that, perhaps even in small quantities, enters as a costituent in the glasses. After revealing the effect of spontaneous fission in glasses, we developed a systematic method of recording the spontaneous fission fragments using large proportional counters of 200 cm lenght and 26 cm width (see fig. 3). The inner surface of the counters was covered with a layer of the material investigated of (2.5-3.0) mgr/cm$^2$ of thickness and of total weight around 50 gr. Layers of the glass material were introduced in the counters, in which tracks of spontaneous fission fragments were revealed and large pulses of fission fragments were recorded, whose number coincides with the one calculated, based on the known volume density of tracks accumulated in the glasses during its existence. In this way, the existence in the glass material of an unknown spontaneously fissionable emitter was confirmed experimentally with the help of an independent method [44]. The statistical accuracy of the experiment is not high, nevertheless the ratio of the effect to the background is satisfactory (about ten). The background experiment was carried out introducing in the counters 35 gr of the electromagnetically separated isotope $^{208}Pb$, which could not contain a mixture of elements with different atomic weight, but could fission by the action of cosmic rays, just as the lead nuclei entering in the constitution of the investigated glasses. In the background experiment only two pulses during 1344 hours of measurement were recorded. The background from uranium spontaneous fission was negligibly small. As it was already said, the uranium concentration in the materials was accurately determined by neutron irradiation, besides these data were controlled by an $\alpha$ -activity measurement with proportional counters during the actual work. These experiments are described with more details in the paper [44].

Following a suggestion by academician A. P. Vinogradov we included among the samples investigated also the iron-manganese nodules — most surprizing formations obtained from the ocean's bed (see fig. 4).

These relatively small round objects of dark-brown colour are millions of years old and are made mainly from iron and manganese and other metals oxides which the nodules extract from the surrounding water. The concentration of some elements (Pb, Te, Hg, W, ...) in nodules is millions of times higher than in the ocean's water. In this way, the natural process of selective extraction of a series of elements from the surrounding medium is realized here. There are some reasons to think, that

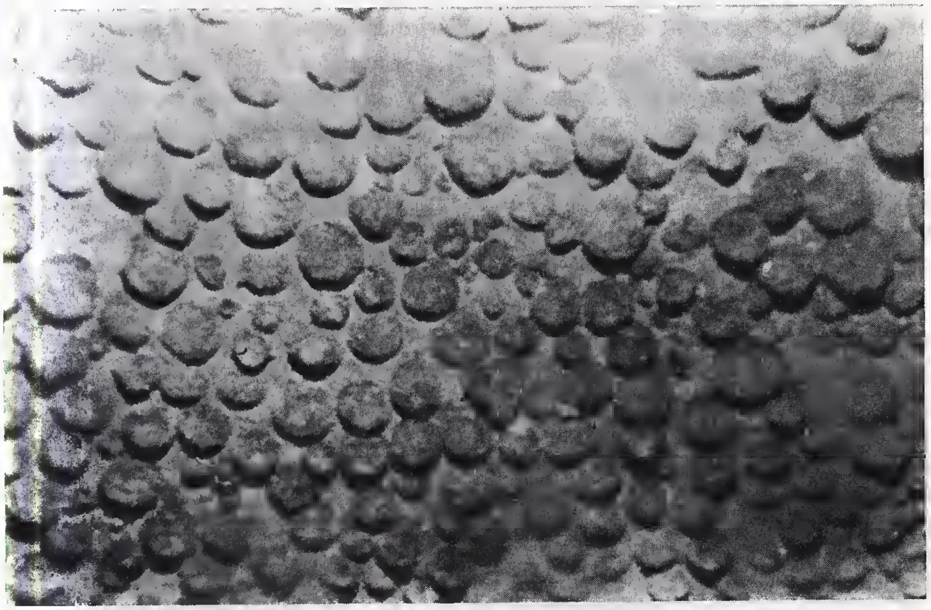

Fig. 4.
A photograph of nodules in the ocean's bed.

also superheavy elements will be contained in the nodulic material in a much higher quantity per unit weight than in the ocean's water. During the actual work with iron-manganese nodules it was discovered that some of them contain relatively small pieces of feldspar, that just like glasses are fission fragments detectors. After a suitable treatment it turned out that on the surface of the feldspar there is a high density of tracks of fission fragments. In the volume of feldspar the density of tracks is significantly lower than on the surface. This means that the spontaneously fissionable emitter responsible for the tracks on the feldspar surface is contained in the nodulic material. The upper limit of the nodule age was determined through the track density of the uranium spontaneous fission in the volume of the feldspar. Knowing the nodule age and determining the uranium concentration in its material allowed one to calculate the

contribution of the uranium spontaneous fission to the number of tracks of fission fragments which is observed on the feldspar surface. It turned out that the uranium spontaneous fission explains less than fifteen percent of the observed effect. On this basis one can suggest the hypothesis, that in the nodule material there is contained besides uranium, some other spontaneously fissionable emitter [45].

Summarizing the results of the above mentioned experiments, it is necessary to say, that we don't have the slightest doubt about the existence of a longlived natural spontaneously fissionable emitter, which is not any of the known spontaneously fissionable nuclei. One may suppose, that the given emitter is either an isotope of a superheavy element from a new region of stability, or a longlived spontaneously fissionable state of one of the known heavy nuclides, on a neutron-enriched isotope of one of the known heavy elements that possess due to any reasons a very high forbiddenes against $\beta_1$-decay.

## 4. On the chemical and geochemical aspects of the search for superheavy elements.

It is necessary to say a few words on the chemical and geochemical aspects of the search for superheavy transuranic elements. When the experimenter reveals in some sample a weak, not accurately enough identified radioactivity, it is natural for him to wish to isolate this radioactivity by chemical operations or at least to enrich the material with that element. We do also have such a desire with respect to the effect of spontaneous fission in some materials which we observed. However, to accomplish the chemical separation of an unknown element is extremely difficult for a series of reasons. Firstly, as indicated above, we cannot at present, on the basis of the existing theory, indicate definitely the $Z$ of the longestlived superheavy element. Secondly, even if the element's $Z$ was known, then the calculation of that element's atom electronic shell structure cannot be carried out with sufficient accuracy. One should take into account that the fundamental properties of the atom will be determined by the configuration of its external electron shell, and for the external weakly bound electrons of such a heavy atom the electron orbits with different quantum numbers have energies very near to each other. Therefore it is quite difficult to solve uniquely the problem of the order of filling of electron shells at such a high $Z$ values, since any, even the most accurate calculation, may neglect some detail, which in this case may be essential. Finally, even if you knew exactly the configuration of the atom electronic shells, you could not just the same consider the

problem solved, since a series of very important chemical and thermodynamical properties of the element are not by far uniquely determined by the structure of the atom external electronic shell.

In connection with the listed difficulties in order to be able to predict the chemical properties of superheavy elements, there remains only the simplest method, which makes use of the known rules of periodicity for the properties of the elements, generalized by Mendeleev. Based on the experimentally determined limit of the actinide family and on the fact that the kurchatovium is the analog of hafnium, it is possible to suggest, as already said, that the elements with $Z = 105\text{-}114$ will be the analogs of the elements from tantalium to lead. According to Mendeleev's terminology the element 114 in this hypothesis may be called ekalead, 110 ekaplatinum and so on. On the basis of the well-known rule of the diagonals it is clear that ekalead, for instance, will be similar in his chemical properties not only to lead, but to some extent to the lead's neighbour on the left — to tallium. Similar considerations may be advanced also relatively to other superheavy elements, however they are so vague that it is impossible to give concrete recomendations about the separation of these elements from materials and geological formations with a very complex composition.

It is very difficult also to answer to the question, in which rocks and in which places of origin one should expect the maximum content of these or other superheavy elements. Even the content of well-investigated elements in different geological formations in a series of cases does not follow the established laws.

One can, however, make the statement that if the superheavy element lives less than $10^8$ years and is present on the earth only because of the arrival of its atoms from the cosmos, then one should look for it in the places where deposits are originated, in continental and ocean waters and in high mountain and antarctic glaciers. The iron-manganese nodules about which we already spoke before, are very convenient in this case for the search of superheavy elements.

If a superheavy element has a lifetime $> 10^8$ years then one can find it both in the basic and in the deposited rocks. The chemistry of this element will determine its content in those or other geological formations. In our experiments with proportional counters we checked a large quantity of the most different minerals and in none of them was detected a high level of content of a spontaneously fissionable emitter, significantly higher than the level of spontaneous fission that we observed in glasses. From this it can be deduced that the abundance of ultraheavy elements in nature is small, and this can be connected either with its radioactive decay (if the lifetime is $10^8$ years $< \tau_{1/2} < 10^9$ years), or with the singularities of the process of synthesis of nuclei of these elements in stars.

## 5. Some prospects for the development of the work on the search of far off transuranic elements.

Since we succeded in revealing the presence in some materials of an unknown spontaneously fissionable emitter it is natural for us to connect the prospects for development of research work on far off transuranic elements with the further investigation of this emitter aiming to determine its $Z$ and $A$ values.

The most direct way of determining the mass number of the emitter is the mass-spectrometric analysis of those materials in which the effect of spontaneous fission has been recorded but does not admit an explanation in terms of the uranium content in these samples. Applying ultrasensitive current measurement of intensity $10^{-17}\,A$, one may try to reveal ions with a mass $> 280$ using mass-spectrometers. However, with such an experimental arrangement the result may be undetermined due to the different background ion currents in the masss-pectrometer hitting that zone of the spectrometer focal plane where the ions with mass $> 280$ should arrive. The sources for such a background may be: the scattering of ions of the ordinary elements ($A < 238$) on the residual gas and on the mass-spectrometer walls, the presence of complex molecular ions with a mass $> 280$, the formation of ions of secondary origin in the interaction of the ion beams with the atoms of the residual gas.

There is yet another more convenient way of setting up the experiment, based on the assumption that the nuclei of superheavy elements should have a large fission cross-section by neutrons. In this case an weightable amount of material containing the spontaneously fissionable emitter undergoes separation by means of a mass-separator. A collector, set in that part of the focal plane where should arrive the ions with mass $> 280$, after the separation is completed is irradiated with an intensive neutron flux in contact with the dielectric detector of fission fragments. The fact that the fission fragment tracks are present in the detector, demonstrates the presence in the collector of an element that fissions under the action of neutrons and the coordinates of the place in the collector around which are grouped the tracks of fission fragments gives the mass number of the fissionable element. Such a way of setting the experiment was discussed in M. Israel's talk at the conference [46]. The sensitivity of this method may be very high, but there are a few limitations: 1) the materials of the collector and of the detector of fission fragments should contain only a very small quantity of uranium and thorium, otherwise the fission of these element nuclei by neutrons will create a high background; 2) during the separation in the mass-separator it is necessary

to create the conditions for the atomic and molecular uranium and thorium ions coming from the source not to fall in the collector in the zone of mass $A > 280$; 3) the integral neutron flux during the irradiation is limited by the radiation damage effect on the detector of fission fragments. For different materials the limiting admissible neutron flux depends not only on the type of material but also on the spectrum of the utilized neutrons. Plastic detectors are the least stable to the damaging action of the neutron flux. The use of a very clean flux of thermal neutrons allows one to increase the limiting admissible integral flux of neutrons to $10^{17}$ — — $10^{18}$ $l/cm^2$, even for plastic detectors. However, the far off transuranic element that is of interest may not fission with thermal neutrons or have a very small fission cross-section. Therefore it is necessary to consider the case of irradiation with fast neutrons. To estimate the sensitivity of the method described one should make a series of assumptions. If the fission cross-section by neutrons of the far off transuranic element equals 1 barn, then separating with the mass separator 10 gr. of matter with an efficiency of 10% and irradiating the collector with an integral flux of $10^{17}$ p/cm², it is possible to reveal a concentration of $5 \cdot 10^{-14}$ gr/gr of this element in matter. In this case the collector and the dielectric materials should contain not more than $10^{-12}$ gr/gr of natural uranium using thermal neutrons and not more than $5 \cdot 10^{-12}$ gr/gr of uranium and thorium working with 2-3 Mev neutrons. The numbers concerning the purity of the materials are indicative, they depend essentially on the resolving power of the mass-separator and on other details of the experiment.

As we recently learned [47], a group working in prof. Bernas' laboratory in France, carried out similar experiments subjecting to separation in the mass separator samples of galenite and gold-containing materials. A significant number of tracks of fission fragments were observed in the detector after neutron irradiation, but they apparently come from the background and are connected with an insufficient purity of the uranium materials. In the conditions of the experiment it would have been possible to obtain information about the presence of a superheavy element in the collector, if one assumed that this element mainly fissions in three or four fragments of comparable mass. However, it seem to us, that this assumption has very little support and this kind of experiments should be developed along the line of increasing the purity of the materials and decreasing the background contributions.

It is also possible to carry out experiments with materials separated in the mass-separator trying to reveal the superheavy elements by the method is lowered. For this purpose it is necessary either a higher concentration of the superheavy element in the material investigated, or larger quantities of the matter (= 1000 gr.) that undergoes separation.

However, the requirement that the collector and detector be clean from uranium becomes in this case significantly less severe.

Another real possibility of obtaining information about the $Z$ value of the spontaneously fissionable emitter consists in the measurement of the average number of neutrons arising in the act of fission of this emitter. It is well known that the number $\bar{\nu}$ rises steeply as the $Z$ of the spontaneously fissionable nucleus increases, for $^{238}$U being $\bar{\nu} = 2.0$ and for $^{252}$Cf being $\bar{\nu} = 3.8$. Nix [48] carried out an estimate by extrapolation of the number of neutrons emitted in the act of spontaneous fission of superheavy elements from the new region of stability. High values of the number $\bar{\nu}$ were obtained, thus for instance for the spontaneous fission of the nucleus $^{298}$114 one predicts a number $\bar{\nu} = 10.5$. Quantitatively, the accuracy of such extrapolations seem to us very low, in particular in Nix's calculation a series of assumptions were made, which may not correspond to the real situation. It was already indicated above, that at present the question about the mass distribution of the fragments from the superheavy elements spontaneous fission is completely unclear and consequently it appears impossible to calculate the energy release in the elementary fission act and the kinetic energy of the fragments. In spite of that, the tendency of the number $\bar{\nu}$ to increase with increasing $Z$ value of the fissionable nucleus should apply qualitatively also to the superheavy elements, i.e. for superheavy elements $\bar{\nu}$ should be larger than 4-5 but not necessarily at all 10.5 as indicated by Nix for $^{298}$114.

From the viewpoint of experimental possibilities, the planning of experiments to measure the number $\bar{\nu}$ for a spontaneously fissionable emitter of the type mentioned above is absolutely feasible. One can reach an efficiency of detection for the act of spontaneous fission near unity, by insuring a geometry of neutron counts near $4\pi$ using a large number of counters. The sensitivity of the experiment in this case may be significantly higher than that in the experiments on the detection of fission fragments using proportional counters, since into the arrangement detecting neutrons it is possible to load up a large quantity of the material investigated (tens of kilograms).

If the efficiency of the arrangement is sufficiently high, then with a definite probability every act of spontaneous fission will be marked by the simultaneous detection of two or more neutrons. The number $\bar{\nu}$ may be easily determined from the experimentally measurable ratio of the probability of simultaneous detection of two, three and so on neutrons.

Performing such experiments the most difficult problem turns out to be the suppression of the background. Especially dangerous is the background due to cosmic rays. Energetic particles interacting with the nuclei of matter may in one collision produce a large number of par-

ticles among which there may be neutrons. Such events of multiple production of neutrons by cosmic particles will simulate in this arrangement the events of spontaneous fission of nuclei.

It seems doubtless, that in spite of the above mentioned difficulties experiments to measure the number $\bar{\nu}$ for the natural spontaneously fissionable emitter which we discovered and experiments to determine the mass number of this emitter using an electromagnetic separator will be realized. The results of these experiments will probably clarify the question of the nature of this emitter. If it will be proved that this emitter is in fact the isotope of a superheavy element, then marvellous prospects for the further development of nuclear physics and chemistry will be opened. The investigation of the elements from the new region of stability will make it possible to widen in an essential way the limits of the periodic system of elements and to check the validity of Mendeleev's law of periodicity for the new eighth period. Besides, the discovery of superheavy elements will mean that they are synthetized in cosmic objects, and this fact is important for the understanding of the processes taking place in stars and star-like formations.

And yet in conclusion one should stress that the problem of observing superheavy elements in nature is an extremely complex problem. This compels to consider of utmost importante the planning of experiments and the interpretation of their results.

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# État heptavalent du neptunium et du plutonium et problème de la valence des actinides.

Le problème de la valence et d'autres propriétés des actinides attire actuellement une très grande attention. A présent sont mis au point les réactions nucléo-chimiques de l'obtention des isotopes à longue durée de vie de plusieurs transuraniens ce que fait complètement accessible leur étude et leur application pratique dans les quantités macroscopiques. Pour les actinides éloignés, moins stables dans cette rangée, il est devenu possible l'étude de leurs propriétés par la méthode des porteurs.

Le neptunium et le plutonium, les premiers transuraniens synthétisés, occupent une position-clef dans le VII période du système périodique des éléments. Une étude plus profonde de leurs propriétés permettra écarter plusieures difficultés, liées avec le placement des actinides dans le système périodique. Le problème de la valeur supérieure de la valence de neptunium et de plutonium est d'un intérêt particulier.

Au premier stade de l'étude des transuraniens on supposait que l'élement n. 93 doit être un analogue au rhénium et lui était donné le symbole le EkaRe.

A l'irradiation de l'uranium par les neutrons lents E. Fermi et ses collaborateurs (1935) ont reçu une substance radioactive, ayant la periode de 13 minutes qui se coprecipitait avec le rhénium et fut prise pour un élément de nombre atomique 93.

O. Hahn, L. Meitner et F. Strassmann (1937) ont obtenu à l'irradiation de l'uranium des substances radioactives se déposant avec le rhénium, l'osmium, l'iridium, le platine et l'or, toutefois chez les « analogues » du rhénium et de l'iridium l'on observait les périodes différentes.

Après la découverte par O. Hahn et F. Strassmann du processus de la fission de l'uranium (1939), il est devenu évident que les transuraniens supposés sont en effet les fragments des noyaux de l'uranium.

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En même temps parmi les produits radioactifs artificiels, obtenus par O. Hahn, L. Meitner et F. Strassmann après l'irradiation de l'uranium par les neutrons, se trouvait une substance ($T_{1/2} = 23$ min.) qui était émetteur $\beta$ et par les propriétés chimiques coincidait avec l'uranium.

On supposait que c'est l'uranium-239. Sa désintégration devait donnez l'origine à l'élement n. 93:

$$^{239}_{92}U = {}^{293}_{93}93 + \bar{\beta} .$$

O. Hahn et ses collaborateurs croyaient que l'élément n. 93 ressemble aux éléments du groupe VII du système périodique, est un analogue du rhénium et devait se déposer par l'hydrogène sulfuré dans la solution acide. Pourtant leurs expériences sur la révélation de l'ekarhenium n'avaient pas de succès. Ils ont supposé que l'élement n. 93 est un émetteur $\beta$ à une grande période. Probablement, une vraie raison de leur échec fut une petite puissance de la source des neutrons.

En 1940 E. MacMillan et P. Abelson ont découvert l'élément n. 93 appelé le neptunium, Np, à l'irradiation des couches minces de l'uranate de l'ammonium par un flux puissant des neutrons obtenus au moyen du bombardement de la cible du berillium par les deutons à l'énergie 16 MeV dans un grand cyclotron de l'Université de Californie. Les fragments obtenus à la fission de l'uranium sont enlevés en résultat du phénomène du recul. Dans la préparation uranique on a découvert deux espèces des activités $\beta$ à $T_{1/2} = 23$ min. et 2,3 jours. La nature de la première était connue: elle appartenait à l'uranium-239. La transformation du premier émetteur au deuxième était une preuve de la formation de l'élément n. 93. E. MacMillan et P. Abelson ont établi que le neptunium forme au moins deux degrés de l'oxydation. Dans l'inférieur d'eux le neptunium est analogique aux éléments des terres rares, dans le supérieur — à l'uranium. Il suit de là que le neptunium n'est pas analogue au rhénium. Par la suite pour le neptunium on a indiqué l'existence des valeurs de la valence suivantes: 6, 5, 4 et 3.

A la désintégration $\beta$ du néptunium s'ensuivait attendre la formation de l'élément n. 94. Il fut désigné par le plutonium, Pu. Son premier isotope $^{238}Pu$ ($T_{1/2} = 89,6\ a$) fut synthétisé à la fin de 1940 par G. Seaborg, E. MacMillan, J. Kennedy et A. Wahl par la méthode du bombardement de l'uranium par les deutons dans le cyclotrone. En qualité du produits intermédiaire on obtenait $^{238}_{93}Np$ ($T_{1/2} = 2,1\ j$). L'étude des propriétés du nouvel élément a démontré que le plutonium, comme le neptunium, peut présenter plusieurs formes de l'oxydation. A l'état de la valence supérieure le plutonium est pareil à l'uranium, mais plus facile à être réduit. Les propriétés des composés de la valence inférieure ressemblent au tho-

rium et aux éléments de terres rares. Par conséquent, le plutonium ne peut être considéré comme un analogue à l'osmium et à d'autres éléments du groupe VIII du système périodique. Les valeurs de sa valence connues jusqu'à présent sont 6, 5, 4 et 3.

Après la découverte encore de quelques transuranies G. Seaborg a fait une supposition (1945) que dans la quatrième grande période du système de Mendéléev après l'actinium commence un groupement d'éléments analogiques aux lanthanides, qu'il a désigné comme les actinides. La théorie des actinides prévoit une analogie entre les éléments correspondants des familles des lanthanides et des actinides.

Dans le nombre des cas la théorie des actinides était confirmée expérimentalement. Par exemple, on a établit une grande ressemblance des transuraniens éloignés avec les éléments de terres rares du sous-groupe de l'yttrium. Pourtant l'application formelle de la conception d'actinides aux thorium, protactinium et uranium demandait une analogie de ces éléments respectivement aux cérium, praséodyme et néodyme ce que ne se réalisait pas dans la pratique. Outre cela, les actinides moyens — l'américium, le curium et le berkélium — se trouvaient capables former des combinaisons à une valence supérieure que le 3 et par cela ils se diffèrent des lanthanides correspondants.

En conformité avec la loi périodique de Mendéléev les actinides ne devaient pas être complétement identiques aux lanthanides. Ils peuvent avoir certaines distinctions des lanthanides ce qui apparait, en particulier, dans la formation des combinaisons à une valence plus haute, surtout par les premiers représentants de cette famille. Or, les essais d'obtenir les combinaisons du neptunium à une valence 7 et du plutonium aux valences 7 et 8 ne sont pas désespérés.

En 1967 les collaborateurs de l'Institut de la chimie physique de l'Académie des sciences de l'URSS N. N. Krot et A. D. Guelman étaient les premiers qui ont marqué du progrès dans cette direction. Ils utilisaient la préparation du neptunium-237 (émetteur $\overline{\beta}$, $T_{1/2} = 2{,}2$ millions d'années), purifiée par la méthode de l'échange ionique. On étudiait l'action de l'ozone sur le neptunium hexavalent dans le milieu alcalin. En choisissant des conditions de l'expérience on prenait en considération le fait qu'avec la croissance de pH, les propriétés d'oxydation des anions oxygénés, une forme plus probable de l'existance du neptunium (VII), diminuent brusquement. Quant à l'ozone il est un très fort oxydant dans les milieux acides comme dans les milieux alcalins.

Les résultats expérimentaux ont montré qu'en faisant passer $O_3$ à travers la suspension des neptunates de potassium ou de sodium dans $0{,}5 - 3{,}5M$ des alcalis, les précipités se dissoudent successivement en formant des solutions vertes intense colorées.

Un spectre d'absorption de telles solutions (fig. 1) se caractérise par les bandes de l'absorption de la lumière aux maximum à la longueur des ondes 412 et 625 m$\mu$.

Le processus de la coloration des solutions ozonisés de neptunium dans la partie visible est soumis à la loi Lambert-Beer et pratiquement ne dépend pas de la concentration des alcalis et du temps de l'ozonisation. Lors de la conservation de longue durée on peut observer la disparition successive de couleur vert des solutions, suivie à une grande concentration de neptunium par le dépôt des neptunates. La vitesse de la décoloration diminue avec l'augmentation de la concentration OH-ions. Ainsi, pendant 5 jours à la température à l'intérieur l'absorption de la lumière ($\lambda$ — 625 m$\mu$) par la solution ozonisée de neptunium en 0,005 et 3,3M NaOH est diminué à 85% et 10% respectivement.

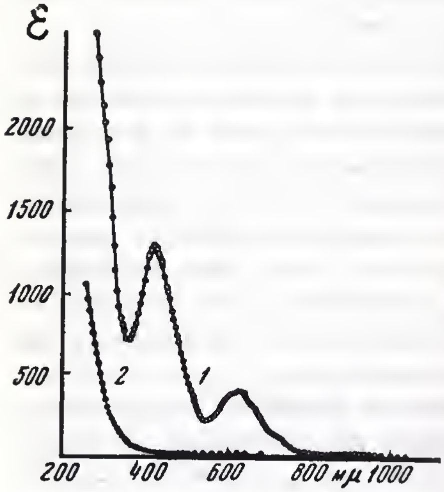



Fig. 1.

Spectres d'absorption du neptunium ozonisé dans 2,4 M NaOH (1) et du neptunium (VI) dans 5 M $HClO_4$ (2); $t = 25°$.

A l'acidification des solutions ozonizées de neptunium leur couleur vert pratiquement disparaît instantanément. Il en résulte, que dans les solutions ozonizées le neptunium est présent ne pas en forme des combinaisons peroxydées puisque celles-ci, se décomposent au milien acide avec la formation du neptunium (V). Il est à noter que les solutions alcalines de perneptunates ont une couleur jaunâtre-rouge.

Le produit d'interaction du neptunium (VI) avec $O_3$ se réduit par l'étain (II), l'hydrazine, l'hydroxylamine, l'eau oxygénée, mais pratiquement ne réagit pas avec les iodide-oxalate-ions. Parmi les réactifs énumérés $H_2O_2$ se distingue par ce qu'elle ne reduit pas le neptunium (VI) dans les milieux alcalins. Grâce à cela il devient possible de déterminer un équivalent d'oxydation du neptunium ozonisé par la dépense de $H_2O_2$ sur son reduction jusqu'au neptunium (VI). Les résultats du titrage spectrophotométriques ont montré (fig. 2), que pour la désoxydation d'un g-atom du neptunium ozonisé on dépense strictement 1 g-équivalent de $H_2O_2$.

On a déterminé aussi un équivalent d'oxydation du neptunium ozonisé par rapport à HJ. Pour cela à un volume mesuré de la solution ozonisée du neptunium d'une concentration certaine on ajoutait la sura-

bondance de KJ, acidifiait par $H_2SO_4$ et l'on titrait $J_2$ degagé par le thiosulfate de potassium. Comme on a établi par les mesures spectrophotométriques dans la solution finale le neptunium ne se trouvait que dans un état pentavalent. Les résultats des expériences ont montré que la

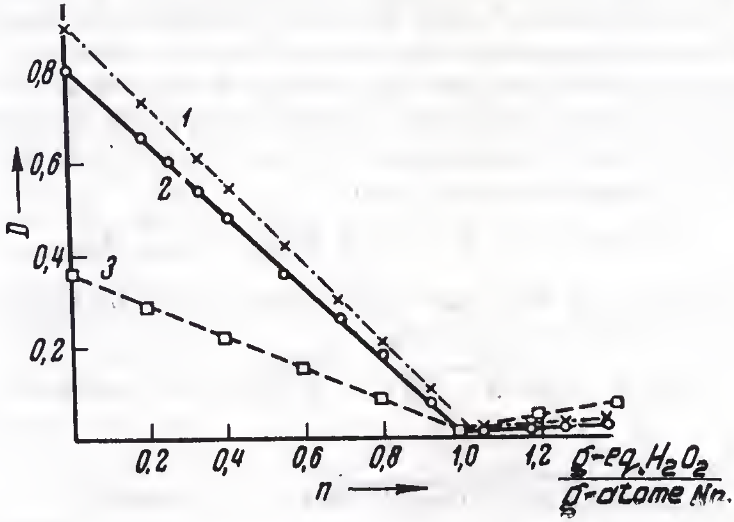



Fig. 2.

Changement de densité optique des solutions du neptunium ozonisé à l'addition de $3{,}3 \cdot 10^{-2}$M $H_2O_2$, épaisseur d'une couche absorbante la lumière 0,3 cm, $t = 25°$.

1 — $C_{Np} = 6{,}65 \cdot 10^{-3}$M,
$C_{NaOH} = 2{,}5$M, $\lambda = 500$ mμ; 2 — $C_{Np} - 6{,}65 \cdot 10^{-3}$M,
$C_{NaOH} = 2{,}5$M, $\lambda = 625$ mμ; 3 — $C_{Np} = 3{,}0 \cdot 10^{-3}$M,
$C_{NaOH} = 0{,}3$M, $\lambda = 625$ mμ.

quantité de $J_2$, dégagé à la reduction du neptunium ozonisé par l'acide iodhydrique jusqu'au neptunium (V) est égal à 2 g-éq. sur 1 g-atome du Np.

On peut commenter les données expérimentales citées ci-dessus de deux points de vues:

1. Le neptunium (VI) forme dans les milieux alcalins avec l'ozone une combinaison, dans laquelle sur les 2 atomes de Np tombe une moylécule de $O_3$.

2. Le neptunium (VI) à une haute valeur de pH est oxydé par l'ozone jusqu'à l'état heptavalent.

Dans la littérature il y a de descriptions de combinaisons de l'ozone avec les métaux alcalins. On les considère comme des sels de la compo-

sition $Me^+O_3^-$. Ils sont en forme de la substance en poudre rouge ou jaunâtre, ils sont plus au moins stables à l'état sec et solubles sans décomposition dans l'ammoniaque liquide.

Au contact avec de l'eau les ozonides se décomposent impétueusement en formant $O_2$ et de l'alcali correspondant. Le produit de l'interaction du neptunium (VI) avec $O_3$ par ses propriétés et sa composition n'à aucune ressemblance aux ozonides des éléments alcalins.

Pour la résolution définitive du problème de l'état de la valence du neptunium ozonisé on a déterminé le rendement d'$O_2$ lors de son interaction avec $H_2O_2$. En cas de combinaison avec l'ozone pour 1 gr-mol de $H_2O_2$ réagissant se dégagerait 2 g-mol de $O_2$:

$$2K_2NpO_4 \cdot O_3 + H_2O_2 = 2K_2NpO_4 + 2O_2 + H_2O\,. \tag{1}$$

A l'oxydation de $H_2O_2$ par le neptunium (VII) le rendement de $O_2$ devrait être moindre de deux fois:

$$2KNpO_4 + 2KOH + H_2O_2 = 2K_2NpO_4 + O_2 + 2H_2O \tag{2}$$

ou

$$2K_3NpO_5 + H_2O_2 = 2K_2NpO_4 + O_2 + 2KOH\,. \tag{2'}$$

Les données reproductibles d'une analyse gazométrique ont montré que dans les limites d'une erreur des expériences ($\pm 5\%$), à 1 g-mol de $H_2O_2$ entré dans la réaction avec l'abondance du neptunium ozonisé, se dégage 1 g-mol de $O_2$.

Sur cette base on peut affirmer avec assurance, que dans les milieux alcalins le neptunium (VI) s'oxyde par l'ozone jusqu'à l'état heptavalent et passe en solution sous forme d'anion coloré.

A côté du neptunium on a étudié aussi l'interaction de l'uranium et du plutonium hexavalents. Comme il fallait attendre la suspension des uranates de potassium et de sodium ne réagit pas dans les alcalis avec l'ozone. Quant au plutonium hexavalent il se conduit par rapport à $O_3$ analogue au neptunium (VI).

Il est vrai que les solutions verte-noires du plutonium ozonisé ont un peu différent spectre de l'absorption (fig. 3). En particulier, il y manque une bande isolée de l'absorption de la lumière au maximum de 412 m$\mu$. Une grande ressemblance des spectres de l'absorption du plutonium et du neptunium ozonisés n'apparaît qu'aux longueurs des ondes plus de 600 m$\mu$.

Il est intéressant à noter que les solutions alcalines récemment préparées à une concentration basse du plutonium (VI) (celui-ci se trouve dans telles solutions principalement sous une forme d'ion) ont de spectres

aux particuliéres bandes très étroites de l'absorption dans le domaine infrarouge le plus proche. Comme on sait, de telles bandes sont causées par la présence chez le plutonium (VI) de deux de 5f-èlectrons [2].

A l'ozonisation des solutions alcalines les bandes étroites de l'absorption du plutonium (VI) disparaissent complètement. Ce fait peut servir l'un des preuves du changement de l'état valent du plutonium (VI) à son interaction avec l'ozone. Les propriétés du plutonium ozonisé (son attitude à l'acidification, aux reducteurs etc.) sont identiques aux propriétés du neptunium (VII). On peut en conclure que dans les milieux alcalins le plutonium (VI) s'oxyde aussi par l'ozone jusqu'à l'état héptavalent.

Un trait particulier des solutions du plutonium (VII) est une instabilité à la conservation. Dans conditions comparables la les vitesse de l'autodésoxydation du plutonium (VII) est plus grande de 2 ordres que dans le cas du neptunium (VII). Une instabilité relative du plutonium heptavalent, probablement est conditionnée par que sa formation passe par le détachement d'un des deux 5f-électrons dont que possède le plutonium (VI).

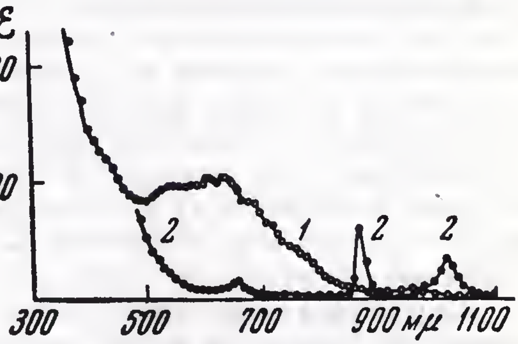



Fig. 3.

Spectres d'absorption des solutions du plutonium (VI) en 0,5 M NaOH avant et après l'ozonisation; $t = 25°$. 1 - plutonium ozonisé; 2 - plutonium (VI) - avant l'ozonisation.

On a établi que le neptunium et le plutonium heptavalents forment avec les cations des éléments alcalino-terreux et des terres rares les combinaisons peu solubles. La composition de ceux-ci et leurs propriétés seront décrits ci-dessous.

Ultérieurement [3] les conditions du passage du neptunium par la méthode de l'ozonisation à l'état heptavalent étaient étudiées plus en détail ce qui permit obtenir son premier composé en état solide.

L'étude s'effectuait avec l'utilisation des solutions azotiques du neptunium-237 purifié par la méthode de l'échange ionique. L'oxydation du neptunium jusqu'à l'état hexavalent s'effectuait par le chauffage des solutions après l'addition de $HNO_3$ jusqu'à la concentration supérieure de 4 M. L'achènement d'oxydation s'était avéré spectrophotométriquement.

Les solutions de travail de KOH et de NaOH étaient préparées des réactifs correspondants d'une marque c. p. et avant l'utilisation furent ozonisées pour la destruction des additions éventuelles des désoxydants.

L'hydroxyde de sodium sans carbonate-ions fut obtenu par la solution dans le courant d'argon du sodium métallique dans le bidistillate. Pour éviter la contamination de la solution par le silicium on effectuait la dissolution dans un récipient en argent.

Pour obtenir l'ozone on utilisait l'ozoniseur de laboratoire à travers duquel on faisait passer l'air sec, purifié de $CO_2$ par les absorbeurs alcalins. Le rendement de l'ozoniseur était près de 10 1-*h* du mélange d'air à la concentration de $O_3$ 15-20 mg-1.

L'oxydation du neptunium s'effectuait par la méthode suivante. Dans la cellule pour l'ozonisation on introduisait une certaine quantité de la solution azotique du neptunium (VI) et passait l'ozone pendant 15-20 min. à la température de l'intérieur pour l'oxydation complète des agents réducteurs eventuels et du neptunium (V). Ensuite on ajoutait à la solution un volume mesuré de l'alcali et l'on continuait à passer l'ozone jusqu'à la disparition du dépôt des neptunates se dégageant lors de l'alcalinisation. On transversait la solution finale dans una fiole jaugée et portait le volume jusqu'à la marque par l'eau ou l'alcali étendu. Dans les cas où l'ozonisation se terminait par la dissolution incomplète des neptunates, on séparait les dépôts des solutions par le centrifugeage.

La pratique a montré que la vitesse de la dissolution de la suspension dépend très fortement de ce qu'à quel point le passage préliminaire du neptunium à l'état hexavalent est complète. La présence même peu considérable de quantités de neptunium (V) mène à une diminution brusque du rendement du neptunium soluté. C'est pour cette raison avant l'alcalinisation il est nécessaire passer l'ozone à travers la solution acide du neptunium (VI) pendant 15-20 min.

Une influence considérable sur la vitesse de l'ozonisation du neptunium exerce aussi sa concentration, la concentration de l'alcali dans la solution et de l'ozone dans le mélange gazeux. A l'augmentation de la concentration du neptunium et la diminution du contenu $O_3$ la vitesse relative du processus de l'ozonisation diminue. La concentration optimale de l'alcali à l'ozonisation est de 2-4M. Dans ces conditions l'ozonisation complète du neptunium (VI) à son contenu de $2.10^{-3}$ g-at-1 s'effectue pendant 15-20 min.

Les solutions à la concentration du neptunium ozonizé 10 g-1 on peut obtenir en passant l'ozone (20 mg-1) à travers la suspension de neptunates dans le 3 M alcali pendant 3-5 heures. Ils sont relativement stables. A la concentration de l'alcali de 4-5 M on peut les conserver pendant quelques mois. A mesure de l'abaissement de la concentration $OH^-$-ions, la stabilité des solutions diminue.

Dans les milieux acides la couleur verte du neptunium ozonisé disparaît pratiquement en un instant. En même temps on peut observer

aux assez hautes concentrations du neptunium le dégagement apparent du gaz. Les mesures spectrophotométriques ont montré que dans les solutions ozonisée après l'acidification, le neptunium passe en état hexavalent. Nous allons examiner certaines particularités de ce processus ci-dessous.

Le neptunium (VII) est un très fort oxydant. A l'absence des désoxydants il passe successivement à l'état hexavalent. On a établi par les études expérimentaux que le neptunium (VI) est reduit vite par hydrazine, hydroxylamine, acide ascorbique, ferrocyanide-ions, solutions alcalines de l'étain et du plomb bivalents. Toutes les réactions avec la participation du neptunium ozonysé prouvent un état heptavalent de ce dernier.

TABLEAU I.

*Valeurs de coéfficients molaires d'extintion des solutions ozonisées du neptunium à 25°.*

| Concentration NaOH, M | Temps de l'ozonisation (en heures) | E à $\lambda = 410$ mμ | E à $\lambda = 460$ mμ | E à $\lambda = 500$ mμ | E à $\lambda = 625$ mμ |
|---|---|---|---|---|---|
| 0,21 | 3 | 1375 | 900 | 474 | 392 |
| 1,0 | 3 | 1415 | 910 | 470 | 386 |
| 1,4 | 3 | 1348 | 885 | 451 | 387 |
| 1,9 | 3 | 1357 | 897 | 456 | 385 |
| 3,1 | 3 | 1350 | 880 | 427 | 381 |
| 5,0 | 3 | 1330 | 866 | 430 | 372 |
| 1,0 | 5 | 1390 | 889 | 470 | 385 |
| 1,0 | 8 | 1405 | 877 | 468 | 390 |

On a fait des essais de dégager de combinaisons solides dont la composition comprend les ions de neptunium (VII). Les expériences ont montré que le neptunium heptavalent forme des combinaisons peu solubles avec les ions des éléments alcalino-terreux et des terres rares et avec un nombre d'autres cations à haute charge. A l'état pur ou a réussi dégager la combinaison du neptunium (VII) avec le cation $Co(NH_3)_6^{3+}$. Pour l'obeenir sous forme gros cristallin fut convenable une méthode suivante:

Au volume de 10 ml 0,5-1M NaOH on ajoutait simultanément, goutte par goutte en agitant bien la solution du neptunium (VII) dans 1-2M alcali à la concentration du métal 3-5 g/l et 0,05-0,1M solution aqueuse de $Co(NH_3)_6Cl_3$. La correlation des concentrations molaires de réactifs au moment la leur réunion doit être proche à 1 : 1. Après l'addition de tout neptunium la solution finale avait un coloris jaunâtre à cause d'une

surabondance peu considérable des ions $Co(NH_3)_6^{3+}$. On séparait le dépôt de la solution d'eau-mer par le centrifugeage et on le lavait 2 fois par l'eau. Ensuite le dépôt était porté à un filtre de verre, y lavé par l'acétone et l'éther et séché en air.

La combinaison formée à l'interaction de $Co(NH_3)_6Cl_3$ avec le neptunium (VII), se dégage à une défécation rapide sous forme d'un dépôt cristallin d'une couleur noire. La couche mince de ce dépôt a une couleur verte foncée. La vue des cristals sous microscope est présentée sur la fig. 4.

Fig. 4.

Photographie de cristaux de la combinaison formé par $Co(NH_3)_6^{3+}$ avec le neptunium (VII) (× 160).

En état sec la combinaison est stable dans le temps. Elle se dissoud peu dans l'eau, mais au contact de longue durée avec l'eau elle se décompose et l'ion $Co(NH_3)_6^{3+}$ passe dans la solution. Dans les alcalis en cas d'absence des ions libres $Co(NH_3)_6^{3+}$ la combinaison est apparamment soluble. La couleur verte de la solution indique à l'état heptavalent du neptunium dans la combinaison.

A la conservation dans le dessiccateur le poids de la substance obtenue ne change pas. La perte du poids au chauffage apparaît de 60°. A la température de 95° après 5 heures la diminution du poids des préparations atteint 10%. Par la suite le poids reste constant. La perte mentionnée du poids est conditionnée, probablement, par le détachement de l'eau présente dans la combinaison.

Le chauffage graduel jusqu'à 110° mène à la décomposition de la combinaison. Le cauffage à la température de 700-800° jusqu'au poids constant se termine par la formation du mélange des oxydes $Co_3O_4$ et $NpO_2$.

Dans le tableau n. 2 sont donnés les résultats des analyses de trois préparations desquels il s'en suit que $Co(NH_3)_6^{3+}$ dépose le neptunium (VII) en forme de la combinaison $Co(NH_3)_6NpO_5 \cdot nH_2O$. La valeur *n* pour les préparations aéroseches est proche à 3. Il n'est pas exclu pourtant que prémordialement se dépose un produit à un plus haut contenu de l'eau, qui dans l'un ou l'autre degré se perd au lavage du dépôt par l'acétone.

TABLEAU II.

*Résultats des analyses des échantillons du composé du neptunium* (VII) *avec* $Co(NH_3)_6^{3+}$.

| Poids d'échantillon mg | Perte du poids au chauffage au rouge | | Neptunium trouvé | | Co trouvé | |
|---|---|---|---|---|---|---|
| | mg | % | mg | % | mg | % |
| 115,5 | 39,0 | 33,87 | 51,3 | 44,42 | 12,8 | 11,08 |
| 92,8 | 31,7 | 34,17 | 41,0 | 44,18 | 10,3 | 11,10 |
| 94,5 | 32,3 | 34,18 | 42,1 | 44,55 | 10,6 | 11,21 |
| Calculé d'après la formule $/Co(NH_3)_6/NpO_5 \cdot 3H_2O$ | | 34,37 | | 44,53 | | 11,07 |

Ainsi, le neptunium (VII) forme dans la combinaison étudiée avec $Co(NH_3)_6^{3+}$ l'anion $NpO_5^{3-}$. Probablement dans les solutions le neptunium existe aussi dans la même forme. Il est évident que la réaction passant à l'ozonisation des combinaisons du neptunium (VI) dans le milieu alcalin peut être exprimée par l'équation:

$$2NpO_4^{2-} + O_3 + 2OH^- = 2NpO_5^{3-} + O_2 + H_2O\,. \tag{3}$$

Dans l'ouvrage [4] fut étudiée la possibilité de l'obtention du neptunium (VII) par d'autres procédés sans utilisation de l'ozone. Dans ce but on a étudié l'interaction du neptunium (VI) dans les milieux alcalins avec un nombre d'oxydants: combinaisons oxydées d'hexa — et octovalente de xénon, persulfate-, periodate- et perborate-ions, bismuthate de sodium, ainsi que du chlore, brome et iode.

Les expériences se produisaient principalement avec les solutions diluées du neptunium (VI) (concentration $2,5 \cdot 10^{-4}$M), à l'alcalinisation desquelles les précipités de neptunates ne se forment pas.

Il fut établi qu'à l'addition aux solutions du neptunium (VI) en 1M KOH de trioxyde du xénon jusqu'à la concentration $5 \cdot 10^{-3}$M on peut observer à froid l'apparition successive du teint caractéristique vert du neptunium (VII). Dans les conditions mentionnées le processus de l'oxydation du neptunium dure à peu près 3 heures. Le spectre de l'absorption des solutions finales est identique au spectre de l'absorption des solutions du neptunium heptavalent obtenues par la méthode de l'ozonisation.

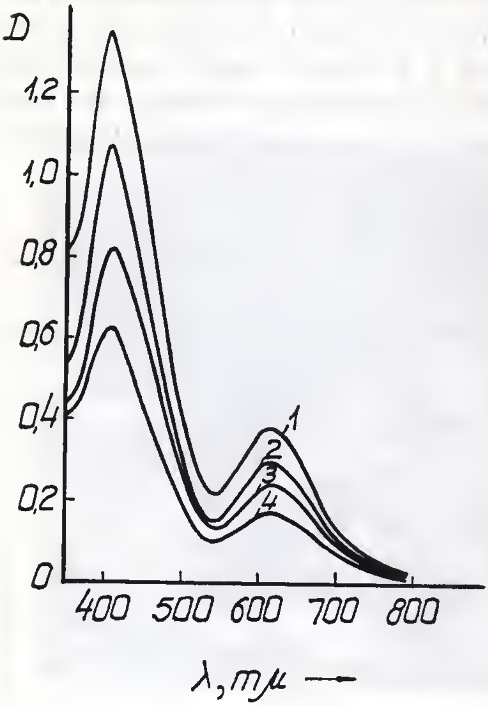



Fig. 5.

Spectres d'absorption des solutions des combinaisons du neptunium (VII), obtenues à l'action de différents oxydants.

Oxydants: 1. Trioxyde de xénon ($C_{Np} = 1,9 \cdot 10^{-4}$M);
2. hypobromite ($C_{Np} = 1,2 \cdot 10^{-4}$M);
3. ozon ($C_{Np} = 1,5 \cdot 10^{-4}$M);
4. périodate ($C_{Np} = 0,9 \cdot 10^{-4}$M).

A l'élévation de la température la vitesse de l'oxydation du neptunium par le xénon (VI) s'augmente brusquement. Ainsi, à la température de 50° le temps de l'oxydation du neptunium (VI) à 50% dans la solution de la concentration $2,5 \cdot 10^{-3}$M de trioxyde du xénon et 1M KOH est égal à 3 min, et à la température de 70° — moins de 4,5 fois. L'abaissement de la concentration de l'alcali jusqu'à 0,25M mène au ralentissement de la réaction approximativement de 1,5 fois.

Il est à noter que l'interaction du neptunium avec le trioxyde du xénon aux températures élevées s'accompagne par le dégagement visible du gaz. C'est déterminé probablement par la décomposition de l'oxyde du xénon d'où il en résulte la formation de l'oxygène gazeu et du xénon. Il n'est pas impossible que l'oxydation du neptunium jusqu'à l'état heptavalent dans une mesure ou l'autre se produit à cause des combinaisons instables des formes valentes inferieures du xénon qui sont des produits intérmédiaires de la décomposition de son trioxyde.

L'oxydation du neptunium jusqu'à l'état heptavalent par perxénonate-ions dans les autres conditions pareilles se produit considérablement plus lentement que dans le cas du trioxyde du xénon. Le semipériode de la réaction dans 1M KOH à la concentration du xénon (VIII) $1.10^{-3}$M et à la température de 70° est 15 min. Comme les mesures spectrophotométriques ont montré, le processus se termine par le passage complète du neptunium à l'état heptavalent. Avec la diminution de la concentration de l'alcali la vitesse de l'oxydation du neptunium s'augmente, ce que correspond au renforcement des propriétés oxydantes et à l'abaissement de la stabilité des perxénonate-ions.

L'interaction du neptunium (VI) dans 0,5M KOH avec les persulfate-ions ne s'effectue assez vite qu'à la concentration relativement haute de l'oxydant et à la température supérieure de 50°. Le produit de la réaction est le neptunium (VII) ce qui était prouvé par les mesures spectrophotométriques. La période de l'oxydation du neptunium (VI) à 50% par la solution du persulfate de potassium 0,1M à la température de 55° est 15 min. Avec l'élévation de la température jusqu'à 70° la vitesse de la réaction s'accroît au quadruple.

Il est intéressant à noter qu'au traitement des précipités fraîchement obtenus des neptunates par les solutions alcalines $K_2S_2O_8$, on peut observer au commencement leur dissolution intensive. Dans ce cas-là on obtient des solutions vertes-foncées avec la concentration du neptunium (VII) jusqu'à 3-5 g/l. Cependant dans un certain laps de temps, selon la température et la concentration de $K_2S_2O_8$, la dissolution des précipités se termine et au chauffage ultérieur des solutions il se voit même un processus inverse de la reduction du neptunium (VII). C'est impossible d'expliquer par l'autodésoxydration du neptunium heptavalent, dont les solutions en absence des oxydants stabilisants ne se changent pas apparemment même et lors du bouillage. Probablement l'instabilité du neptunium (VII) au bouillage avec $K_2S_2O_8$ est déterminé par les produits intermédiaires de la décomposition des persulfates-ions.

A l'interaction du neptunium (VI) dans les milieux alcalins avec le perborate du potassium on obtient les solutions rouges des perneptunates. La réaction se produit très vite au chauffage comme à froid. Evidemment les perborate-ions dans les milieux alcalins se trouvent en équilibre avec $H_2O_2$ qui forme des combinaisons peroxydes avec le neptunium (VI). Puisque l'eau oxygénée est un bon reducteur pour le neptunium (VII) (1), on n'a pas réussi d'obtenir ce dernier à l'aide des perborates.

L'oxydation du neptunium (VI) jusqu'à l'état heptavalent par les périodate-ions se caractérise par une grande dépendance de la concentration de l'alcali. Dans la solution d'une concentration 0,1M de periodate de potassium et 1M KOH la période de l'oxydation du neptunium (VI)

à 50% à la température de 85° est égale à 20 min. A l'augmentation de la concentration de l'alcali jusqu'à 5M dans les mêmes conditions la réaction se termine presque complément pendant 8-10 min. Les solutions diluées du neptunium (VII), reçues par l'oxydation avec les periodate-ions, ont le teint verdâtre-jaune. Après le bouillage de courte durée la teinte des solutions disparaît et elles prennent un teint vert vif typique pour le neptunium heptavalent.

L'oxydation du neptunium (VI) par le bismouthate de sodium dans les solutions alcalines diluées est une réaction hétérogène ne se produisant assez vite qu'à la température d'ébullition. Après l'achèvement de la réaction et la séparation de l'oxydant surabondant par centrifugeage on obtient les solutions colorées ayant un spectre de l'absorption typique pour le neptunium (VII). La méthode de l'obtention du neptunium heptavalent à l'aide de bismouthate de sodium pratiquement est incommode. Cependant au point de vue scientifique l'oxydation du neptunium (VI) par le réactif mentionné représente un certain intérêt.

L'hypochlorite- et hypobromite-ions dans les conditions comparables font passer le neptunium (VI) à l'état heptavalent à peu près à une même vitesse. A 55° et à la concentration des oxydants $2 \cdot 10^{-3}$M la période du semi-achèvement de la réaction en 1 et 0,25M KOH est égale à 10 et 20 min respectivement. A l'élévation de la température à 10° la réaction s'accélère de 2 fois.

Il est à noter qu'on peut utiliser les solutions alcalines du brome pour l'obtention des solutions relativement concentrées du neptunium heptavalent. Les expériences ont montré que les précipités fraîchement déposés des neptunates se dissoudent assez vite en solutions des alcalis 2-3 M, contenant 0,2-0,5 g-ions d'hypobromite. A 60-70° lors de 15-20 min. on obtient des solutions à la concentration du neptunium (VII) 5-6 g/l. Le processus se ralentit dans le temps et habituellement on ne réussit pas obtenir un passage complet de toute la phase solide à la solution. Si séparer un précipité non dissous par le centrifugeage et traîter par une nouvelle portion de la solution alcaline d'hypobromite, on peut observer l'oxydation supplémentaire de neptunium. Pourtant on obtient avec cela les solutions du neptunium (VII) plus diluées.

En distinction au chlore et brome, l'iode dans les milieux alcalins ne réagit pas avec le neptunium (V). Au contraire, les iodide-ions peuvent réduire le neptunium (VII) jusqu'à l'état hexavalent. Il est vrai que cette réaction ne se produit avec la vitesse considérable qu'au chaffage intensive des solutions.

Ainsi, dans les milieux alcalins on peut oxyder le neptunium (VI) jusqu'à l'état heptavalent par l'ozone, persulfate- et periodate-ions, trioxyde du xénon, perxénonate-ions, bismouthate de potassium, hypochlo-

rite- et hypobromite-ions. Dans le tableau 3 est comparée la vitesse de l'oxydation du neptunium (VI) dans les milieux alcalins par des différents oxydants.

TABLEAU III.

*Oxydation de la* $2{,}5.10^{-4}$M *solution du neptunium* (VI) *dans le milieu alcalin par des différents oxydants.*

| NN° | Oxydant (formule du réactif de départ) | Concentration de l'oxydant M | Température °C | Concentration d'ions $OH^-$, g-ions/1 | Période de l'oxydation Np (VI) à 50% min |
|---|---|---|---|---|---|
| 1. | $XeO_3$ | $3 \cdot 10^{-3}$ | 25 | 1,0 | 20 |
| 2. | $XeO_3$ | $2{,}5 \cdot 10^{-3}$ | 50 | 1,0 | 3 |
| 3. | $XeO_3$ | $2{,}5 \cdot 10^{-3}$ | 50 | 0,25 | 5 |
| 4. | $XeO_3$ | $2{,}5 \cdot 10^{-3}$ | 70 | 1,0 | 0,7 |
| 5. | $Na_4XeO_6 \cdot nH_2O$ | $1 \cdot 10^{-3}$ | 70 | 1,0 | 15 |
| 6. | $Na_4XeO_6 \cdot nH_2O$ | $1 \cdot 10^{-3}$ | 70 | 0,25 | 8 |
| 7. | $K_2S_2O_8$ | 0,1 | 55 | 0,5 | 15 |
| 8. | $K_2S_2O_8$ | 0,1 | 70 | 0,5 | 4 |
| 9. | $KJO_4$ | 0,1 | 85 | 1,0 | 20 |
| 10. | $KJO_4$ | 0,1 | 85 | 5,0 | 1,5 |
| 11. | $NaBiO_3$ | (10 g/l) | 95 | 1,0 | 5 |
| 12. | KClO | $2 \cdot 10^{-2}$ | 55 | 1,0 | 8 |
| 13. | KClO | $2 \cdot 10^{-2}$ | 55 | 0,25 | 15 |
| 14. | KBrO | $2 \cdot 10^{-2}$ | 55 | 1,0 | 10 |
| 15. | KBrO | $2 \cdot 10^{-2}$ | 55 | 0,25 | 20 |
| 16. | KBrO | $2 \cdot 10^{-2}$ | 70 | 1,0 | 3 |

A pH = 14, à la température = 25° et l'activité des réactifs égale à 1, les redox potentiels maxima et minima des réactifs mentionnées sont en limites 1,24 et 0,75 *v* respectivement pour les pairs $O_3/O_2$ et $BrO^-/Br_2$. Il est évident, que le redox potentiel de la paire Np(VII)/Np(VI) dans les mêmes conditions est moins de 0,76 *v*, mais plus de 0,40 *v* puisque dans 1M KOH le neptunium (VI) s'oxyde par KBrO, mais n'entre pas en réaction avec $O_2$. Les mésures immédiates du potentiel d'électrode de platine en 1M solution KOH à une même concentration du neptunium (VI) et du neptunium (VII) $2 \cdot 10^{-4}$M ont donné 0,61 *v* (à $t = 25°$). Cette valeur, probablement, est proche à la valeur du potentiel formel de la paire Np(VII)/Np (VI) malgré sa reversibilité.

Outre des méthodes décrites ci-dessus on peut obtenir le neptunium (VII) d'une manière de l'oxydation électrochimique du neptunium (VI) sur l'anode de platine.

Il est évident que le neptunium heptavalent dans les solutions alcalines aqueuses à froid n'est pas enclin en général au détachement de

l'oxygène. Cependant il réagit facilement avec plusieures combinaisons, ayant des propriétés des réducteurs. Parmi certaines d'elles on mentionnait déjà l'eau oxygénée qui ne fait passer le neptunium (VII) qu'à l'état hexavalent. Cette réaction est strictement stoechiométrique et se produit avec une grande vitesse. Pour la réduction de 1 g-at du neptunium (VII) on dépense 0,5 g-m $H_2O_2$.

Le ferrocyanide de potassium, hydrazine, hydroxylamine acide ascorbique, étain (II) et le neptunium (V) sont aussi au nombre des réducteurs qui réduisent pratiquement instantanément le neptunium (VII). Toutes ces combinaisons sauf le dernier, sont capables de passer le neptunium (VII) non seulement à la forme hexa-mais aussi à pentavalente.

Pourtant le plus souvent par la métode spectrophotomètrique on peut établir à une précision suffisante la stoechiométrie des réactions de réduction du neptunium (VII) jusqu'à l'état hexavalent. Il s'est trouvé avec cela que le neptunium (VII) réagit avec la ferrocyanide dans la rélation molaire de 1 : 1, avec l'hydrazine et l'acide ascorbique — 1 : 0,25, avec l'étain (II) — 1 : 0,25 et avec le neptunium (V) — 1 : 1. La réaction du neptunium (VII) avec l'hydroxylamine se traduit par l'équation aux coéfficients fractionnaires. Probablement, $NH_2OH$ s'oxyde par le neptunium (VII) dans les deux ou plusieures réactions parallèles.

Le neptunium (VII) est stable par rapport aux ions de $Cl^-$, $Br^-$, $CH_3COO^-$ et à la temperature ambiante dans l'intervalle de la concentration $OH^-$ 0,3-3 g-ions/l ne se réduit pas pratiquement par nitrite-, oxalate-, étylènediamine tetracétate-ions, ammoniac, alcool et acétone. Avec la solution 0,2M de sulfite de sodium à $t = 25^0$ et à concentration de l'alcali plus de 1M le neptunium (VII) réagit très lentement. Cependant dans les solutions d'alcalis plus diluées et au chauffage la vitesse de la réaction s'accoroît brusquement. Comme l'ont montré les études cinétiques, cette réaction qui est autocatalitique, se produit suivant la manière suivante:

$$\mathrm{Np(VII)} + \mathrm{SO_3^{2-}} \xrightarrow{K_1} \mathrm{Np(VI)} + \mathrm{SO_3^-} \text{ lentement}$$

$$\mathrm{Np(VII)} + \mathrm{SO_3^-} + \mathrm{H_2O} \longrightarrow \mathrm{Np(VI)} + \mathrm{SO_4^{2-}} + 2\mathrm{H^+} \text{ vite}$$

$$\mathrm{Np(VI)} + 1/2\mathrm{SO_3^{2-}} + 1/2\mathrm{H_2O} \longrightarrow \mathrm{Np(V)} + 1/2\mathrm{SO_4^{2-}} + \mathrm{H^+} \text{ lentement}$$

$$\mathrm{Np(VII)} + \mathrm{Np(V)} \longrightarrow 2\mathrm{Np(VI)} \text{ vite.}$$

La valeur de la constante $K_1$ à $t = 25$, $\mu = 0,5$ et $OH^- = 0,37$ g-ions/l est trouvée égale 0,60 l/mol-min. A la première approximation $K_1$ est inversement proportionel à $[OH^-]^2$.

Le processus de la réduction du neptunium (VII) par les ions $SO_3^{2-}$ s'accroît fortement en présence des microquantités de certains métaux de la valence variable. Ainsi les additions $KMNO_4$ même à la concentration $5 \cdot 10^{-7}M$ accélèrent la réaction de 2 fois. On observe un effet analogue à l'introduction dans la solution des microquantités des combinaisons du cobalt et du cuivre.

Dans la solution avec $[OH^-] \geq 0,5$ g-ions/l le neptunium (VII) ne se réagit pas avec 0,1M KJ même au faible chauffage. Pourtant la situation se change brusquement lors du passage aux solutions diluées des alcalis. Ainsi, en 0,1M KOH le neptunium (VII) se réduit par 0,1M KJ assez vite même à froid. Cette réaction, comme dans le cas $SO_3^{2-}$ est autocatalytique et s'accélère fortement à l'introduction des microadditions $KMnO_4$ ainsi que des sels du cobalt et du cuivre.

Les conditions de l'obtention du plutonium (VII) furent aussi étudiées plus en détail [5]. Dans les solutions à la concentration KOH ou NaOH 0,5-3M le plutonium (VI) s'oxyde jusqu'à l'état heptavalent par l'ozone, les persulfate-ions et par la méthode électrochimique, mais ne réagit pas avec les combinaisons du xénon, périodate, hypochlorite, hypobromite et bismouthate de sodium.

L'oxydation du plutonium (VI) par l'ozone se passe habituellement plus vite que dans le cas des neptunates. Dans les solutions à la concentration du plutonium (VI) $0 \cdot 02M$ et NaCH 2-3M pour l'achèvement pratiquement complète de la réaction il suffit pas plus de 30 min. La haute vitesse de l'oxydation, probablement s'explique par la dissolution considérable des plutonates dans les solutions alcalines. Le rendement du plutonium (VII) à l'interaction de l'ozone avec les plutonates est proche à 100%.

Les persulfate-ions n'oxydent le plutonium (VI) qu'à la température proche à l'ébullition de la solution. La concentration optimale de l'alcali est égale à 0,5 — 1M. Le degré de l'oxydation du plutonium (VI) par le 0,1 — 0,2M persulfate de potassium habituellement ne dépasse pas 50% Le rapport du plutonium hexavalent aux oxydants dépend fortement de la concentration d'ions $OH^-$. A l'augmentation de celle-ci la formation du plutonium VII se facilite à l'abaissement brusque de ses propriétés oxydantes. En résultat le plutonium (VI) dans les solutions assez concentrées des alcalis commence à réagir avec tels oxydants relativement faibles comme hypochlorite, hypobromite et perxenonate-ions.

L'oxydation du plutonium par hypochlorite et hypobromite devient sensible dans les solutions à la concentration de l'alcali de 5M et davantage. En 6,5M NaOH, à $t = 95^\circ$ et à la concentration $NaBrO = 0,1M$ le rendement maxima du plutonium (VII) est observable dans 10-15 min et atteint 30%. En 13M alcali le plutonium (VI) s'oxyde par 0,1M hypo-

bromite pratiquement quantitativement et la réaction prend sa fin à 80° déjà dans 10 min.

Les perxénonate-ions n'oxydent le plutonium (VI) que dans solutions fortes de KOH. Dans les solutions concentrées de NaOH dégage le précipité insoluble de perxénonate de sodium et le plutonium (VII) ne se forme pas. A la température de 95° et à la concentration de perxénonate de 0,02M le degré de l'oxydation du plutonium (VI) en 11M KOH atteint 30% dans 15 min. et reste ensuite sans changement considérable.

Sur la base des données suivant les méthodes de l'obtention du plutonium (VII) il suit que le potentiel redox de la paire Pu(VII)/Pu(VI) à $t^o = 25^o$ et pH = 14 se trouve plus de 0,76 v, mais moins de 1,24 v.

Les mesures du potentiel de l'électrode en platine dans les solutions du plutoniums (VII) n'ont pas donné de résultats reproductibles. Probablement le platine est un fort catalyseur de la réaction de la réduction du plutonium (VII) par l'ion d'oxygène jusqu'à l'état hexavalent. Grâce à ce fait dans la couche adjacente à l'électrode la contenance du plutonium (VII) ne correspond pas à sa concentration dans la solution.

Il est intéressant à noter que les solutions alcalines du plutonium (VI) fraîchement préparées ont un spèctre typique aux bandes étroites de l'absorption (voir, fig. 3). Celles-ci après l'oxydation du plutonium (VI) disparaissent complètement. A cet égard le passage du plutonium de l'état hexavalent à celui heptavalente est analogue au passage du neptunium (V) au neptunium (VI).

Contrairement au neptunium, le plutonium à l'état heptavalent est instable. La vitesse de sa réduction dans les milieux aqueux dépend fortement de la concentration d'ions $OH^-$. Dans 1M NaOH à $t = 25^o$ la $5 \cdot 10^{-3}$M solution du plutonium (VII) passe à 50% à l'état hexavalent dans 8 heures. Dans les mêmes conditions mais à la concentration de l'alcali 0,1M, la semipériode de la réaction ne dure plus que 50 min. seulement.

Le plutonium (VII) réagit plus énergiquement que le neptunium (VII) avec les réducteurs différents. Par la méthode du titrage spectrophotométrique on a établi que les premiers stades de l'interaction du plutonium avec $H_2O_2$, $N_2H_4$ et $K_4Fe(CN)_6$ sont des réactions suivantes:

$$\mathrm{Pu(VII)} + 1/2\mathrm{H_2O_2} \rightarrow \mathrm{Pu(VI)} + \mathrm{H^+} + 1/2\mathrm{O_2}$$

$$\mathrm{Pu(VII)} + \mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Pu(VI)} + \mathrm{Fe(CN)_6^{3-}}$$

$$\mathrm{Pu(VII)} + 1/2\mathrm{N_2H_4} \rightarrow \mathrm{Pu(VI)} + 1/2\mathrm{N_2} + 2\mathrm{H^+}\,.$$

A l'addition de la surabondance des réducteurs le plutonium passe dans les formes valentes plus basses.

Le plutonium se réduit vite et complètement aussi par hydroxylamine, acide ascorbique, combinaisons de Sn(II) et Pb(II), ions $J^-$, $JO_3^-$. Par rapport à ces deux derniers réactifs le plutonium se distingue du neptunium (VII) considérablement. On peut prendre cette distinction pour base de la détermination analytique spectrophotométrique du plutonium et neptunium heptavalents lors de leur présence en commun.

Dans les solutions à la concentration de l'alcali 0,5M et plus le plutonium (VII) ne réagit pas avec $Cl^-$ — et $Br^-$ mais se réduit par l'ammoniac. La réaction avec $NH_3$ à la température ambiante se produit lentement.

Le dernier temps on a réussi obtenir de nouvelles combinaisons du neptunium (VII) à l'état solide, et dégager aussi la première préparation du plutonium (VII) [5]. La tâche se compliquait par le fait qu'à hautes valeurs de pH la plupart des ions métalliques se précipitent en forme de hydroxydes et plusieurs cations complexes se décomposent.

La combinaison du neptunium (VII) avec $/Pt(NH_3)_5Cl/^{3+}$ est pareille en beaucoup de choses à celle décrite ci-dessus, $/Co(NH_3)_6/NpO_5 \cdot nH_2O$. Elle se dépose sous forme du précipité épais vert foncé à l'addition lente au neptunium (VII) en 1M NaOH de la solution aqueuse saturée de $[Pt(NH_3)_5Cl]Cl_3$. Après le lavage par l'alcool et le séchage en l'air la combinaison par sa composition correspond à la formule $/Pt(NH_3)_5Cl/NpO_5$. Le précipité a une structure cristalline ce qui était prouvée par la méthode des rayons-X. Les echantillons du produit synthétisé sont stables à la conservation prolongée dans dessiccateur. Dans l'eau et les solutions diluées de l'alcali la combinaison n'est pas pratiquement soluble. Au chauffage jusqu'à 100° se produit la décomposition de la substance avec le dégagement de l'ammoniac.

Si au neptunium (VII) ajouter la solution saturée de $Ba(OH)_2$ dans 0,5 M NaOH on peut observer le dégagement du précipité amorphe vert sale, dont la composition se traduit par la formule $Ba_3(NpO_5)_2 \cdot nH_2O$. Pour obtenir cette combinaison à l'état pur il est nécessaire entreprendre exprès les mesures particuliers pour que les carbonate-ions ne tombent pas dans les solutions du processus. A l'état sec les preparations $Ba_3(NpO_5)_2 \cdot NH_2O$ se conservent sans changement au cours de plusieurs jours. Dans les milieux alcalins la combinaison est visiblement soluble. Le produit de la solubilité dans 1M NaOH à $t = 20°$ est trouvé égal à $2 \cdot 10^{-18}$. Par les alcalis forts $Ba_3(NpO_5)_2 \cdot nH_2O$ se décompose en faisant passer le neptunium (VII) dans la solution et avec la formation simultanée du précipité $(BaOH_2)$.

Les ions de strontium déposent le neptunium (VII) de 0,5 — 1M NaOH sous forme du précipite brun-verdâtre floconneux de composition $Sr_3(NpO_5)_2 \cdot nH_2O$. Par son aspect comme par ses propriétés les plus

importants les combinaisons du neptunium (VII) avec $Ba^{2+}$ et $Sr^{2+}$ sont très pareils. Une particularité distinctive de $Sr(NpO_5)_2 \cdot NH_2O$ est sa solubilité élevée dans les solutions diluées des alcalis.

Obtenir à l'état solide les combinaisons du plutonium heptavalent il fut plus difficile que dans le cas du neptunium (VII). Cela est liée à ce que le plutonium (VII) est un fort oxydant et se réduit facilement par les cations complexes $/Co(NH_3)_6/^{3+}$ et $/Pt(NH_3)_5Cl/^{3+}$ (probablement an dépense des molecules intrasphériques de $NH_3$). Celles-ci, par conséquence, ne conviennent pas pour déposer le plutonium (VII).

A l'état pur on n'a réussi [5] junqu'à présent qu'à dégager la combinaison du plutonium (VII) aux ions $Ba^{2+}$. Son synthèse s'effectuait d'une manière suivante. A l'aide de l'ozone on préparait 0,1M solution du plutonium (VII) dans 2 M NaOH exempt de $CO_3^{2-}$. On la diluait avec de l'eau deux fois et on ajoutait 0,1M $Ba(NO_3)_2$ à raison de maintenir dans la solution au dessus de précipité la concentration $Ba(OH)_2$ telle quelle ne surpassât sa solubilité. On séparait vite le précipité par le centrifugeage, on lavait par 0,1M NaOH et analysait sur le plutonium et le barium.

Le composé de barium et plutonium (VII) se déposait sous forme du précipité noir-brunâtre amorphe, dont la composition correspond à une formule $Ba_3(PuO_5)_2 \cdot nH_2O$. Se trouvant sous la solution d'eau-mère la combinaison se décompose graduellement aux dépens de transition du plutonium à l'état hexavalent. La décomposition est observable aussi dans le cas du traitement des précipités par les alcalis forts. Le barium reste alors sous forme d'insoluble hydroxyde, et le plutonium (VII) passe dans la solution. Par les propriétés $Ba_3(PuO_5)_2 \cdot nH_2O$ est très parèil à la combinaison correspondante du neptunium (VII). Sa particularité spécifique est une instabilité élevée à la conservation.

Arrêtons-nous sur les formes de l'existence du neptunium (VII) et de plutonium (VII) dans les solutions aqueuses. Comme l'on mentionnait ci-dessus, le spectre de l'absorption du neptunium (VII) ne dépend pas de la méthode de son obtention et de la composition de la solution alcaline. Il en resulte qu'à hautes valeurs de pH le neptunium (VII) n'existe que dans une forme ionique. Cette forme est un anion $NpO_5^{3-}$, comme il s'en suit des données de synthèse des combinaisons solides du neptunium (VII).

Le fait de la formation de l'anion stable $NpO_5^{3-}$ à première vue paraît un peu inattendu. Le fait est que les éléments dans le degré de l'oxydation 7 existent, habituellement sous forme d'ions $\mathcal{E}O_4^-$ et $\mathcal{E}O_6^{5-}$ à coordination tétraédrique et respectivement octaédrique de l'oxygène. Les anions du type $O_5^{3-}$ quoique connus (le cas d'iode) (VII), mais ils ne sont qu'une forme peu stable intermédiare entre les ions tetraédriques et octaédrique.

Ainsi, le neptunium à l'état heptavalent par forme d'existence dans les milieux alcalins se distingue considérablement des autres éléments du groupe 7 du système périodique de Mendéléev. Probablement il est necessaire d'en chercher la cause dans les particularités de la chimie des éléments à l'enveloppe éléctronique remplissant sa couche 5f.

L'un des traits typiques des transuraniens est leur penchant pour la formation de la liaison forte avec deux atomes d'oxygène dans tous les états valents supérieurs de trois [2]. Ainsi, presque toutes les combinaisons du neptunium, plutonium et américium hexa- et heptavalents dans les solutions et à l'état solide sont de dérivée des ions correspondants de type $MeO_2^{2+}$ et $MeO_2^+$. D'autre part le principale et le plus stable composé des oxydes d'éléments mentionnés correspond à une formule $MeO_2$ malgré que pour l'américium l'état tétravalent est généralement peu typique. En outre même dans le cas de curium on a obtenu un oxyde $CmO_2^6$.

Si on étend une particularité mentionnée ci-dessus des transuraniens sur leur état heptavalent, on peut considérer l'ion $NpO_5^{3-}$ comme forme d'anion d'hydrooxyde $NpO_2(OH)_3$. Celui-ci doit ainsi avoir des propriétés amphotères. Dans les alcalis suivant la réaction:

$$NpO_2(OH)_3 + 3OH^- \rightarrow NpO_5^{3-} + 3H_2O$$

on obtient l'anion $NpO_2^{3-}$ et dans les acides on peut attendre la formation du cation $NpO_2^{3+}$:

$$NpO_2(OH)_3 + 3H^+ \rightarrow NpO_2^{3+} + 3H_2O\ .$$

Pour confirmer expérimentalement la supposition de l'existence d'hydroxyde de $NpO_2(OH)_3$ et de cation $NpO_2^{3+}$ on a étudié la conduite du neptunium (VII) à l'acidification de ses solutions alcalines. Les expériences ont montré qu'à l'addition de la surabondance de l'acide le teint vert des solutions du neptunium (VII) devient instantanément jaunâtre-brun. L'alcalisation inverse des solutions acides mène au rétablissement de leur teint vert. Les mesures spectrophotométriques ont montré qu'après l'acidification rapide et l'addition réitérative de la surabondance de l'alcali dans les solutions le neptunium se trouve à létat heptavalent. Donc, le changement du teint des solutions du neptunium (VII) au passage des milieux alcalins à ceux d'acide du moins au moment initial est conditionné par le changement de la forme d'existence du neptunium (VII).

Les résultats d'expériences décrites concordent bien à la conjecture de l'existence du neptunium (VII) dans les solutions acides sous forme de cation $NpO_2^{3+}$ dérivé de l'hydroxyde $NpO_2(OH)_3$. Celui-là fut obtenu selon la méthode suivante [5].

A la solution du neptunium (VII) on additionnait 4-5M $HNO_3$ exempt des nitrite-ions à raison de la neutralisation de la masse principale de l'alcali. Ensuite la solution était neutralisée jusqu'à pH 9-5. Un precipité noir se déposait. On le séparait vite de la solution d'eau mère par le centrifugeage, lavait avec l'eau et puis analysait.

Les résultats d'analyses ont montré que des solutions du neptunium (VII) dans les limites de pH 5-9 se dégage la combinaison dont la formule $NpO_2(OH)_3$. L'admixtion du neptunium (VI) dans les dépôts habituellement ne dépasse pas 2-3%.

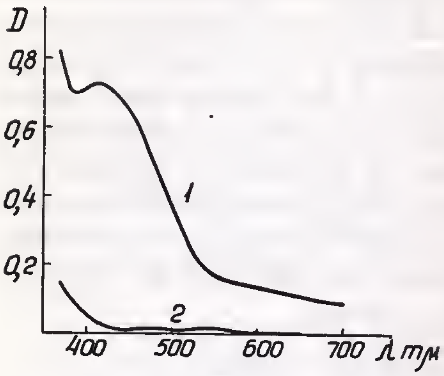



Fig. 6.

Spectres d'absorption du neptunium hexavalent et heptavalent dans 0,5M $HNO_3$; $l = 5$ cm. 1 – $3{,}4 \cdot 10^{-4}$M solution Np (VII) (les données sont trouvées par extrapolation pour le moment de la préparation de solution); 2 – $3{,}4 \cdot 10^{-4}$M solution de Np (VI).

Les échantillons fraîches de $NpO_2(OH)_3$ se dissoudent vite et complètement dans les alcalis comme dans les acides minéraux.

La solubilité de $NpO_2(OH)_3$ dans l'eau ne dépasse pas 10 mg/l (selon métal). Les solutions acides de $NpO_2(OH)_3$ ont un teint jaunâtre-brun intensif. Dans le spectre de l'absorption des solutions azotates $NpO_2^{3+}$ il y a une large bande à maxima à 410 mμ. Le coéfficient molaire de l'absorption du neptunium (VII) sans 0,5M $NHO_3$ à maxima est égal à 430 l/mol. cm (fig. 6).

Le neptunium (VII) dans les milieux acides est instable dans le temps. La vitesse du passage de $NpO_2^{3+}$ dans le neptungle-ion, $NpO_2^{2+}$ ne dépend pas pratiquement de la concentration de $HNO_3$ dans les limites 0,1-1M. La semi-période de la réaction de la réduction en 0,5M $HNO_3$ à 25° est égale à 5-10 min.

Le redox potentiel de la paire $NpO_2^{3+}/NpO_2^{2+}$ dans les milieux acides est plus que le potential de la paire $O_3/O_2$, i. e. plus de 2,07 v (à 25°, pH = O et à l'activité d'ions 1). Parce que l'ozone n'oxyde pas d'ions de $NpO_2^{2+}$ et n'influence pas sur la stabilité de $NpO_2^{3+}$ dans le temps. La haute valeur du potentiel de la paire $NpO_2^{3+}/NpO_2^{2+}$ a servi d'une cause de ce qu'au travail avec le neptunium dans les milieux acides personne n'a obtenu « par hasard » neptunium (VII).

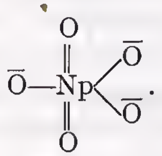
Il est évident qu'il est à envisager le cation $NpO_2^{3+}$ comme un membre final d'une série homologique de $NpO_2^{n+}$ où $n$ se change de

o jusqu'à 3 à l'augmentation de la valence du neptunium de 4 jusqu'à 7:

$$\begin{array}{ccccccc} NpO_2 & — & NpO_2^+ & — & NpO_2^{2+} & — & NpO_2^{3+} \\ \mathrm{IV} & & \mathrm{V} & & \mathrm{VI} & & \mathrm{VII} \end{array}$$

A partir de ça on peut affirmer avec assurance que l'ion $NpO_2^{3+}$ ainsi que le neptunoyle et le neptunyle [2] a une structure linéaire. Ensuite on peut affirmer que la liaison entre le neptunium et l'oxygène dans l'ion $NpO_2^{3+}$ se caractérise par la plus haute énergie et respectivement pas la moins grande distance interatomique que dans le cas de $NpO_2^{2+}$. Cette conclusion, il semble de trouver une confirmation expérimental dans les données préliminaires selon les spectres IR de certaines combinaisons solides du neptunium (VII).

La haute durabilité de la liaison entre les atomes de l'oxygène et le métal dans l'ion $NpO_2^{3+}$ permet à celui-là servir d'une base pour la formation d'anion $NpO_5^{3-}$, dont la structure schématique est la suivante:



Il n'est pas difficile de voir qu'à la formation de $NpO_5^{3-}$ un groupe $NpO_2^{3+}$ reste comme une unité structurale isolée mais ce n'est pas possible dans le cas de la formation d'ions $NpO_4^-$ ou $NpO_6^{5-}$. C'est à cette raison l'anion $NpO_5^{3-}$ est une unique forme stable de l'existence du neptunium (VII) dans les milieux alcalins.

Le plutonium (VII) à l'acidification de ses solutions alcalines passe vite à l'état hexavalent. C'est pourquoi on n'a pas encore réussi à dégager à l'état solide la combinaison $PuO_2(OH)_3$ ou obtenir les solutions, contenantes le cation $PuO_2^{3+}$.

Dans les milieux alcalins le plutonium (VII) existe sous la forme d'anion $PuO_5^{3-}$ qui par ses propriétés principales est un analogue complet de $NpO_5^{3-}$. Il est évident, que dans la structure d'ion $PuO_5^{3-}$ entre un groupe $PuO_2$ qu'on peut prendre pour un membre d'une série homologue

$$\begin{array}{ccccccc} PuO_2 & — & PuO_2^+ & — & PuO_2^{2+} & — & PuO_2^{3+} \\ \mathrm{IV} & & \mathrm{V} & & \mathrm{VI} & & \mathrm{VII} \end{array}$$

Le plutonium (VII) a une telle particularité qu'à l'état libre le cation $PuO_2^{3+}$ ne peut pas probablement exister dans les milieux aqueux parce qu'il passe très vite à l'ion $PuO_2^{2+}$.

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La découverte de l'ètat heptavalent du neptunium et du plutonium fait voir dans un nouvel aspect le problème de la valence des actinides. Comme l'a montré un matériel mentionné ci-dessus il n'est pas exclu une possibilité d'obtenir des combinaisons du plutonium octavalent. L'existence de l'américium hexavalent dans les solutions fut établie depuis longtemps [7]. Il y avait une publication qui affirmait la formation du curium (VI) à l'ozonisation du curium (III) dans la solution d'acétate-tampon [8]. Bien que les résultats de cet ouvrage furent par la suite refutés [9], on ne peut pas encore considérer le problème de la valence supérieure du curium définitivement résolu.

L'application formelle de la théorie d'actinides exigeait une analogie complète entre les actinides et les lanthanides correspondants, en premier lieu — selon leur valence. Cette condition se montrait irréalisable aux proches actinides (Th-Pu). On supposait que les actinides moyens et éloignés ne manifesteront que leur trivalence. Cependant il y en avait aussi des écarts. Bientôt après la dècouverte du curium et du berkélium on a ètabli qu'ils peuvent passer à l'état quadrivalent. Ce fut surtout étonnant pour le curium, un analogue du gadolinium. Celui-ci ne montre dans ses combinaison que la trivalence.

TABLEAU IV.

*Valence des lanthanides et des actinides*

| Lanthanides | | | Aktinides | | |
|---|---|---|---|---|---|
| Symbole chimique | Numéro atomique | Valence manifestée | Valence manifestée | Numéro atomique | Symbole chymique |
| Ce | 58 | $\underline{3}$, 4 | 3, $\underline{4}$ | 90 | Th |
| Pr | 59 | $\underline{3}$, 4 | 3, 4, $\underline{5}$ | 91 | Pa |
| Nd | 60 | 3 | 3, $\underline{4}$, 5, $\underline{6}$ | 92 | U |
| Pm | 61 | 3 | 3, 4, $\underline{5}$, 6, 7 | 93 | Np |
| Sm | 62 | 2, $\underline{3}$ | 3, $\underline{4}$, 5, $\underline{6}$, 7 | 94 | Pu |
| Eu | 63 | 2, $\underline{3}$ | (2), $\underline{3}$, 4, 5, 6 | 95 | Am |
| Gd | 64 | 3 | $\underline{3}$, 4 | 96 | Cm |
| Tb | 65 | $\underline{3}$, 4 | $\underline{3}$, 4 | 97 | Bk |
| Dy | 66 | 3 | $\underline{3}$, (4) | 98 | Cf |
| Ho | 67 | 3 | 3 | 99 | Es |
| Er | 68 | 3 | 3 | 100 | Fm |
| Tu | 69 | 3 | 2, $\underline{3}$ | 101 | Mv |
| Yb | 70 | 2, $\underline{3}$ | $\underline{2}$, 3 | 102 | No(?) |
| Lu | 71 | 3 | 3 | 103 | Lr |

Le dernier temps on a eu les informations que l'oxyde du californium $Cf_2O_3$ d'une couleur blanche étant chauffé au courant de l'oxygène passe en oxyde coloré sombre probablement du californium (IV) [10].

D'autre part, les études effectuées par la méthode des porteurs sur les microquantités des actinides éloignés, ont montré que le mendélévium ($Z = 101$) trivalent peut être facilement passé en solutions à l'état bivalent [11, 12] quant à l'élement n. 102 cet état est dominant. Les expériences préliminaires effectuées sur un petit nombre d'atomes de lawrencium ($Z = 103$) ont permis de conclure que cet élément probablament,

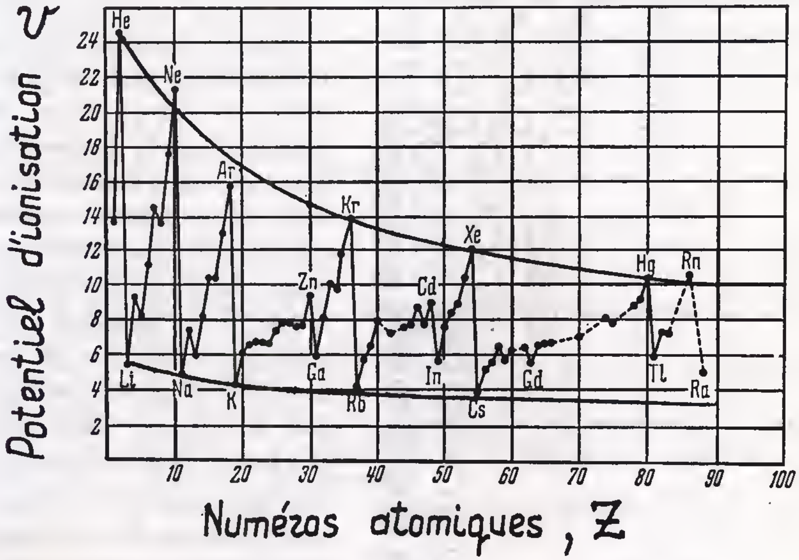


Fig. 7.

Potentiels d'ionisation d'élements (selon lexpremier électron).

est stablement trivalent [14], bien qu'il n'est pas exclu une possibilité des réactions de sa réduction ou, au contraire, d'oxydation.

Dans le tableau 4 sont comparées les valeurs actuellement connues de la valence des éléments lanthanides et actinides.

On ne peut pas considérer inattendue la différence observable des propriétés des lanthanides et des actinides et en premier lieu de leur valence manifestée. Elle est tout à fait explicable au point de vue de la loi périodique de D. I. Mendéléev. Dans chaque groupe du système périodique, à mesure d'augmentation des numéros atomiques les éléments-analogues se caractérisent par un certain changement de leurs propriétés physiques et chimiques. C'est observable non seulement pour les éléments

isolés, mais aussi dans le cas de leurs groupements. Comme un exemple peuvent servir les valeurs de potentiels d'ionisation (fig. 7).

Comme on le sait, dans chaque période du système de Mendéléev la valeur supérieure du potentiel d'ionisation corresponde au gaz inerte, et l'inférieure — à l'élément alcalin. Pour les uns comme pour les autres éléments limitrophes les potentiels d'ionisation diminuent à mesure de l'augmentation des numéros atomiques ce qui est lié, sans doute avec l'augmentation des rayons atomiques résultant du remplissage d'enveloppes électroniques de plus en plus eloignées des atomes. Il est important aussi que la différence entre les potensiels d'ionisation du gaz inerte et de l'élément alcalin diminue considérablement au passage à la fin du système périodique. Ce fait explique l'activité chimique élevée des gaz inertes lourds — xénon et radon, ainsi que la capacité des actinides proches et moyens de manifester une valence haute et variée. On peut croire que les actinides éloignées peuvent former aussi des combinaisons de haute valence, bien que dans les conditions habituelles pour eux est caractéristique la valence 3 ou 2.

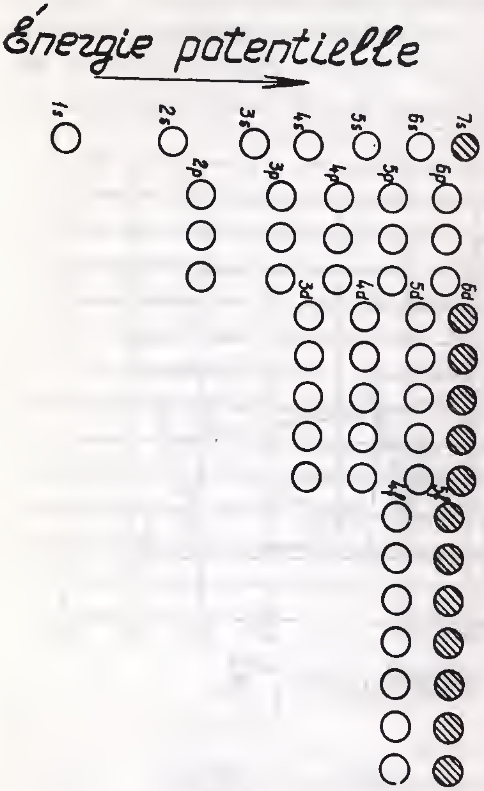


Fig. 8.

Schèma de niveaux énergétiques électroniques dans les atomes des éléments.

1. *les compteurs de fission*, 2. *le filtre*, 3. *la cible.*

Dans la littérature on émettait maint fois des opinions que dans la VII période du système de Mendéléev les niveaux d'énergie des électrons 6d et 5f sont proches l'un à l'autre [15, 16]. C'est illustré par schéma du fig. 8 et sert la cause de ce que dans la famille des actinides, les premiers 5f-électrons n'apparaissent que dans l'uranium métallique et sont absents chez le thorium et le protactinium. Dans les combinaisons peuvent être d'autres relations. Il est établi, par exemple, que les ions de $Th^{+}$ et de $Th^{-}$ n'ont pas 5f-électrons, mais dans l'ion Thì$^{+}$ on trouve un 5f-électron [17].

Dans cet article on ne se donne pas pour tâche étudier des problèmes liés à la valence supposée des éléments qui se trouvent dans le système périodique après les actinides (transactinides). Formellement le kourtchatovium (Z = 104) doit être un analogue de hafnium ou thorium, un élément No 105 — un analogue de tantale etc. Cependant en conformité de la ressemblance énergétique 5f- et 6d- groupes d'électrons on peut attendre que les transactinides vont manifester et une valence anomalement haute à l'image des éléments du sous-groupe de cuivre où la valence élevée est conditionnée par la proximité des niveaux d'énergie de s- et d-électrons extérieurs.

En conclusion on peut dire que la synthèse des éléments transuraniens et la révélation de leurs particularités intéressantes servent au développement suivant et à l'affermissement de la loi périodique de D. I. Mendéléev.

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M. HAÏSSINSKY (*)

# La dixième épreuve subie par le système périodique.

## (La septième période)

Malgré les centaines ou les milliers de volumes, monographies et mémoires qui ont été consacrés à l'histoire, à l'analyse et à l'interprétation du Système Périodique de D. I. Mendéléev, ce sujet, comme toutes les œuvres humaines véritablement grandes, n'est pas épuisé et je ne crois pas qu'il le sera dans un avenir prévisible. Pourtant, sans être remis en question ou contesté sur le fond, il a été pendant le siècle de son existence constamment discuté, diversement présenté et soumis à des épreuves plus ou moins sévères. A ces épreuves appartiennent tant les anomalies, apparentes ou réelles, que présente la classification périodique en certains endroits et dont Mendéléev était parfaitement conscient, que les découvertes de phénomènes imprévus et l'évolution des connaissances sur la matière, qui étaient susceptibles d'ébranler la structure du Système. Je me propose de rappeler ici une dizaine de ces difficultés, celles qui me paraissent les plus importantes et fondamentales et nous verrons que non seulement elles ont été surmontées, souvent en s'éliminant mutuellement au fur et à mesure qu'on parvenait à comprendre leur origine et leur nature, mais qu'en fin de compte le système périodique en sortait plus cohérent, plus riche et plus rationnel. Je vais m'arrêter plus particulièrement sur la dernière épreuve en date, la dixième, toujours actuelle.

1. – Comme première anomalie citons le cas des éléments Cu, Ag, Au qui forment le sous-groupe 1*b* dans le tableau à 8 colonnes et dont l'état d'oxydation maximal est pourtant supérieur à 1. On sait que dans certaines variantes du Tableau Périodique, Mendéléev a placé ces éléments deux fois: après les trois triades (Fe, Co, Ni, Cu etc.) et dans le sous-groupe 1*b*. Vraisemblablement on doit y voir un résultat des hésitations de Mendéléev qui du point de vue chimique, devait considérér ces trois métaux comme une suite naturelle des triades et qui, d'autre

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part, ne voulait pas laisser vide la colonne 1*b*. Cette difficulté disparaît dans le tableau à 18 colonnes, mais nous nous référerons dans cet exposé toujours au tableau « court », à 8 colonnes, qui résume mieux à mon avis, la périodicité des propriétés chimiques.

2, 3 – A côté de cette anomalie verticale, le Tableau Périodique présente deux anomalies horizontales: les trois *triades* et les *lanthanides*. Dans le premier cas, on place trois fois trois éléments différents dans la même colonne; dans le second cas, après de longs tâtonnements, devenus d'autant plus incertains que le nombre des terres rares identifiées augmentait, on a été finalement amené à réunir 15 éléments, il est vrai de propriétés très voisines, dans une seule case.

4 – D'après les poids atomiques, le potassium (39, 100), le nickel (58, 69) et l'iode (126, 91), sont respectivement plus légers que l'argon (39, 944), le cobalt (58, 94) et le tellure (127, 61). Or, d'après leurs propriétés chimiques, les premiers trois éléments sont placés, sans aucun doute possible, *après* les trois autres (*inversions*).

5 – Pour respecter la périodicité, Mendéléev a laissé *12 cases vides* dans son tableau, en prévoyant qu'ils seront remplis par la découverte d'éléments encore inconnus dont il a préconisé les propriétés, souvent avec beaucoup de détails. On sait que ce pari a été brillamment gagné par la découverte de Sc, Ga, Ge, Te, Hf, Re, Po, At, Fr, Ra, Ac et Pa.

6 – Cette dernière liste montre la contribution importante de la *radioactivité* au remplissage des « trous » dans le Tableau Périodique. Mais en même temps, elle a soumis celui-ci à une nouvelle et rude épreuve par la découverte de nombreux autres éléments, une trentaine environ, tels que UX, MsTh, les corps *A*, *B*, *C*, etc., pour lesquels on ne disposait plus de cases vides. La découverte de l'isotopie a permis cependant d'éliminer sans peine cette difficulté.

7 – Il en fut à peu près de même avec la découverte des *gaz rares* qui n'ont pas trouvé, eux non plus, de places disponibles dans le tableau. Ici, la difficulté fut simplement et élégamment surmontée par Mendéléev lui-même et Ramsay qui ont ajouté un groupe o au tableau.

8 – Un danger d'un autre genre guettait l'édifice de Mendéléev, lorsque Moseley a clairement établi la signification fondamentale du *nombre atomique*. La question se posait: une classification basée sur les poids atomiques ne sera-t-elle pas en conflit avec les conséquences qu'on pourrait déduire du nombre atomique? Il n'en fut rien; au contraire, l'introduction de ce nombre a permis d'éliminer la difficulté des inversions et, jointe au principe d'exclusion de Pauli, de limiter le nombre possible des

lanthanides et des radioéléments et de fixer le nombre possible des éléments chimiques, entre l'hydrogène et l'uranium, à 92.

9 – La *structure électronique* des atomes qui aurait pu, elle aussi, se trouver en désaccord avec un système construit empiriquement et à partir uniquement de faits chimiques, a au contraire consolidé le système, expliqué d'abord qualitativement, puis quantitativement la périodicité, les anomalies verticales et horizontales; en bref, elle a donné une base rationnelle à une œuvre, en grande partie, intuitive. Il faut d'ailleurs noter que les configurations électroniques ont été, en général, établies non seulement à l'aide de données spectroscopiques et magnétiques, mais aussi en prenant en considération les propriétés chimiques des divers éléments et la place qu'ils occupent dans le Tableau Périodique.

10 – Mendéléev connaissait seulement 2 éléments dans la septième période, le thorium et l'uranium, et encore, pour les y placer, il a été amené à doubler approximativement leurs poids atomiques. On admettait, en effet, en 1867, Th = 118 et U = 116; le premier élément se trouvait alors associé aux terres rares, et l'uranium au groupe de *B*, *Al* ... trivalents et placé entre Cd et Sn. Mais par un examen approfondi des propriétés chimiques de l'uranium métallique, de ses chlorures et de ses oxydes, Mendéléev aboutit dès 1870 à la conclusion que le poids atomique de l'élément doit être voisin de 240 et l'élément lui-même placé dans la 7ème période comme homologue de Mo et W. Du même coup, l'oxyde UO devenait $UO_2$, $U_2O_3$ devenait $UO_3$ etc. Pour le thorium Mendéléev admit le poids atomique 231 et il l'a placé également dans la septième période comme homologue de Zr. Il développa en 1871 en détail, des arguments en faveur de ces changements dans un manuscrit qui a été publié en 1950 par l'Académie des Sciences de l'U.R.S.S. [1]. Il a prévu de plus, l'existence d'un éka-Ta, dont le premier isotope ($^{234}$Pa ou UX 2) a effectivement été découvert en 1913 par Fajans et Göhring et dont les propriétés chimiques étudiées par la suite, surtout sur $^{231}$Pa, actuellement bien connues, justifient pleinement son homologie avec Nb et Ta.

Cette classification a été universellement reconnue pendant de nombreuses années par le chimistes et les physiciens. Par exemple, dans la variante verticale du tableau périodique, dite de Bohr-Thomsen, les homologues de Th, Pa, U sont respectivement Hf (inconnu des temps de Mendéléev), Ta et W; la *nouvelle série de « terres rares »* dont l'existence résultait de la théorie de l'atome de Bohr, y *est placée après l'uranium*.

On sait que cette situation a radicalement changée depuis la découverte par Seaborg et ses collaborateurs de l'américium et leur faillite

de déceler son état d'oxydation supérieur, Am VI [2]. Ceci a conduit Seaborg à reprendre une hypothèse de Villar [4], selon laquelle la constitution de la sous-couche électronique $5f$ débute au thorium, de même que le premier électron $4f$ apparaît dans le cérium, d'où il résulterait la formation d'une série « d'actinides », analogue à la famille des lanthanides avec la prédominance de la valence III. Selon cette conception, le thorium, le protactinium, l'uranium sont mal placés dans les colonnes IV, V et VI respectives et deviennent homologues de Ce, Pr et Nd.

Après être sorti indemne de toutes les épreuves énumérées plus haut, le système périodique tel qu'il a été conçu par Mendéléev échouerait-il donc dans la dernière épreuve ? En posant cette question, je ne veux nullement insinuer que Mendéléev ne *pouvait* pas se tromper. Etant donné l'état des connaissances physiques de l'époque, il a exprimé parfois des idées qui paraissent actuellement naïves ou erronées [3]. Dans ce qui suit, je vais cependant essayer de démontrer que malgré les succès indéniables de la conception des « actinides », celle-ci est en contradiction avec l'esprit même du système périodique et c'est Mendéléev qui avait raison sur ce point. Nous verrons qu'il est aussi peu raisonnable de considérer Np, Pu et Am comme homologue respectifs de Pm, Sm et Eu.

Pour justifier la conception des actinides on avance des arguments de trois sortes: 1) la présence d'électrons $5f$; 2) la predominence de la trivalence, ce qui d'ailleurs n'est exact que pour la deuxième moitié de la série; 3) Th, Pa et U seraient de « mauvais » homologues de Hf, Ta et W (voir par exemple [4, 6]).

La première série d'arguments, basée implicitement sur l'idée que la configuration électronique définit les propriétés chimiques de l'élément, donc sa place dans le système périodique, a été déjà refutée à plusieurs reprises [7], notamment par C. K. Jorgensen et moi-même [8] et j'y reviendrai au Congrès de Léningrad [9]. Je vais cependant m'y arrêter brièvement ici aussi.

Dans le tableau 1 sont donnés les configurations électroniques et les états d'oxydation des éléments $4f$ et $5f$. L'état d'oxydation le plus stable est écrit en italique, un état d'oxydation qui n'existe que dans les solides est donné entre parenthèses. Les configurations électroniques des cinq derniers éléments de la série $5f$ sont encore hypothétiques, bien que très probables. On voit que tous les lanthanides, à l'exception de Ce, Gd et, peut-être Tb, cas encore discuté, ont la configuration $4f^q6s^2$, c'est à dire qu'électroniquement ils sont des homologues du baryum et non du lanthane qui a la configuration $4f^{q-1}5d^16s^2$; ils seraient donc des « barides » [13]. De même, en partant du même point de vue, l'hélium avec ses électrons $1s^2$ serait l'homologue des alcalino-terreux [14]. Ainsi ce n'est pas tellement le nombre d'électrons de telle ou telle autre catégorie

TABLEAU I

*États d'oxydation et configurations électroniques des éléments 4f et 5f.*

| Éléments | États d'oxydation | Configuration électronique | Éléments | États d'oxydation | Configuration électronique |
|---|---|---|---|---|---|
| Th | *4* ([a]) | $[Rn]6d^27s^2$ | Ce | *3*, 4 ([g]) | $[Xe]4f5d6s^2$ |
| Pa | 4, *5* | $[Rn]5f^26d7s^2$ | Pr | *3*, (4) | $[Xe]4f^36s^2$ |
| U | 3, 4, 5, *6* | $[Rn]5f^36d7s^2$ | Nd | (2), *3* ([h]) | $[Xe]4f^46s^2$ |
| Np | 3, 4, *5*, 6, 7 | $[Rn]5f^46d7s^2$ | Pm | *3* | $[Xe]4f^56s^2$ |
| Pu | 3, *4*, 5, 6, 7 | $[Rn]5f^67s^2$ | Sm | 2, *3* | $[Xe]4f^66s^2$ |
| Am | *3*, 4 ([b]), 5, 6 ([c]) | $[Rn]5f^77s^2$ | Eu | 2, *3* | $[Xe]4f^76s^2$ |
| Cm | *3*, 4 ([b]) | $[Rn]5f^76d7s^2$ | Gd | *3* | $[Xe]4f^75d6s^2$ |
| Bk | 3, *4* | $[Rn]5f^97s^2$ | Tb | *3*, (4) | $[Xe]4f^96s^2$ ([i]) |
| Cf | 2 ? ([d]), *3* | $[Rn]5f^{10}7s^2$ | Dy | *3* ([h]) | $[Xe]4f^{10}6s^2$ |
| Es | 2 ? ([d]), *3* | $[Rn]5f^{11}7s^2$ | Ho | *3* | $[Xe]4f^{11}6s^2$ |
| Fm | 2 ? ([d]), 3 | $[Rn]5f^{12}7s^2$ | Er | *3* | $[Xe]4f^{12}6s^2$ |
| Md | 2, *3* | $[Rn]5f^{13}7s^2$ | Tm | (2), *3* | $[Xe]4f^{13}6s^2$ |
| 102 | 2, *3* ([e]) | $[Rn]5f^{14}7s^2$ | Yb | 2, *3* | $[Xe]4f^{14}6s^2$ |
| 103 | *3* ([f]) | $[Rn]5f^{14}6d7s^2$ | Lu | *3* | $[Xe]4f^{14}5d6s^2$ |

([a]) L'existence de $ThI_3$ a été signalée, mais non confirmée [10]. En tout état de cause, il ne s'agirait pas d'un composé ionique.

([b]) $Am F_4$ et $Cm F_4$ sont solubles dans les solutions concentrées des fluorures alcalins. $Am(OH)_4$ et probablement $Cm(OH)_4$ se dissolvent en solution acide de pyrophosphates [11].

([c]) Am-II se forme à l'état solide dans des conditions particulières.

([d]) L'existence d'un état bivalent nécessite confirmation, notamment à l'échelle macroscopique.

([e]) D'après [12], 102 II serait en solution aqueuse plus stable que 102 III.

([f]) Par extrapolation.

([g]) Il semble que tous les lanthanides puissent, à l'état solide, se former à l'état bivalent dans des conditions très particulières [13].

([h]) Un tétrafluorure est connu.

([i]) Ou $4f^85d^16s^2$.

qui détermine la chimie d'un élément, mais leur qualité, et souvent, d'une façon très complexe. Ceci est d'ailleurs également vrai pour les premiers éléments 5*f*, pour lesquels les étiquettes 5*f* ou 6*d* ne signifient pas, en réalité, grand' chose, si l'on ne connaît pas les niveaux énergétiques auxquels ils correspondent.

En nous adressant maintenant aux deux autres groupes d'arguments en faveur des actinides, qui sont de nature chimique, il importe d'éviter que « les arbres nous cachent la forêt », qu'en nous embrouillant dans

les détails nous perdions de vue l'essentiel. Il me semble alors que pour caractériser un élément, il n'est guère possible de faire un meilleur choix que celui que Mendéléev a adopté pour édifier son système: considérer en premier lieu l'état d'oxydation maximal, puis l'état d'oxydation le plus stable, ensuite le comportement des composés en solution (complexes, solvolyse, oxydoréduction), la structure cristalline, la densité à l'état élémentaire etc. En procédant de cette façon, la classification qu'on en déduit pour des éléments dont la chimie est suffisamment connue, doit naturellement être en harmonie avec la structure électronique, supposée connue elle aussi, ou bien, dans le cas contraire, elle contribuera utilement à la connaître. Un désaccord entre la structure électronique et la chimie ne peut s'expliquer que par une connaissance défectueuse de l'une ou de l'autre, ou encore par l'intervention d'un phénomène inconnu qu'on doit rechercher et interpréter.

La comparaison des états d'oxydation des éléments de la septième période avec ceux des lanthanides a été donnée dans le tableau I. Il semble utile de l'étendre aux éléments de transition de la sixième période, ce qui est fait dans la fig. 1. Un simple regard suffit alors pour se convaincre que les éléments $5f$ occupent une position intermédiaire entre les éléments de transition et les lanthanides dont ils diffèrent considérablement. Pour ces derniers on connaît un seul cas d'un état tétravalent en solution aqueuse, la valence II est rare et III prédomine du commencement jusq'à la fin de la série. Dans la septième période, Th IV est stable et cinq autres états tétravalents existent en solution, sans compter Am IV et Cm IV solubles dans des conditions particulières; comme les éléments de transition, U, Np, Pu et Am ont des valences multiples, la valence III ne prédomine vraiment qu'à partir de Cm, l'état d'oxydation II semble s'installer à la fin de la série.

D'après les critères adoptés il serait trop long de discuter ici le cas du thorium, quadrivalent, si l'on doit le considérer comme homologue de Ce ou de Hf, mais il est évident que le protactinium n'est pas l'homologue du praséodyme et que la chimie de l'uranium a peu à faire avec celle du néodyme. Il en est de même pour Np et Pu dont la chimie est, grâce à leurs multiples états d'oxydation, si riche, si complexe et si différente de la chimie de Pm et Sm. Même l'américium dont l'état d'oxydation le plus stable est III, le même que pour l'europium, diffère profondément de celui-ci, puisque les états d'oxydation *instables* du premier sont 4, 5 et 6, et celui de l'europium est 2. Pour la plupart de ces éléments, il devient presque superflu de comparer les propriétés à l'état d'oxydation caractéristique, puisque celui-ci n'est pas le même dans les deux series: Pa V et Pr III, U VI et Nd III etc. Pour plus de détails voir [7].

En dehors de la multiplicité des valences, notons toutefois quelques autres propriétés qui distinguent les premiers éléments 5*f* des lanthanides et les rapprochent des éléments de transition, notamment des triades: diminution en solution de l'état d'oxydation le plus stable et l'état d'oxy-

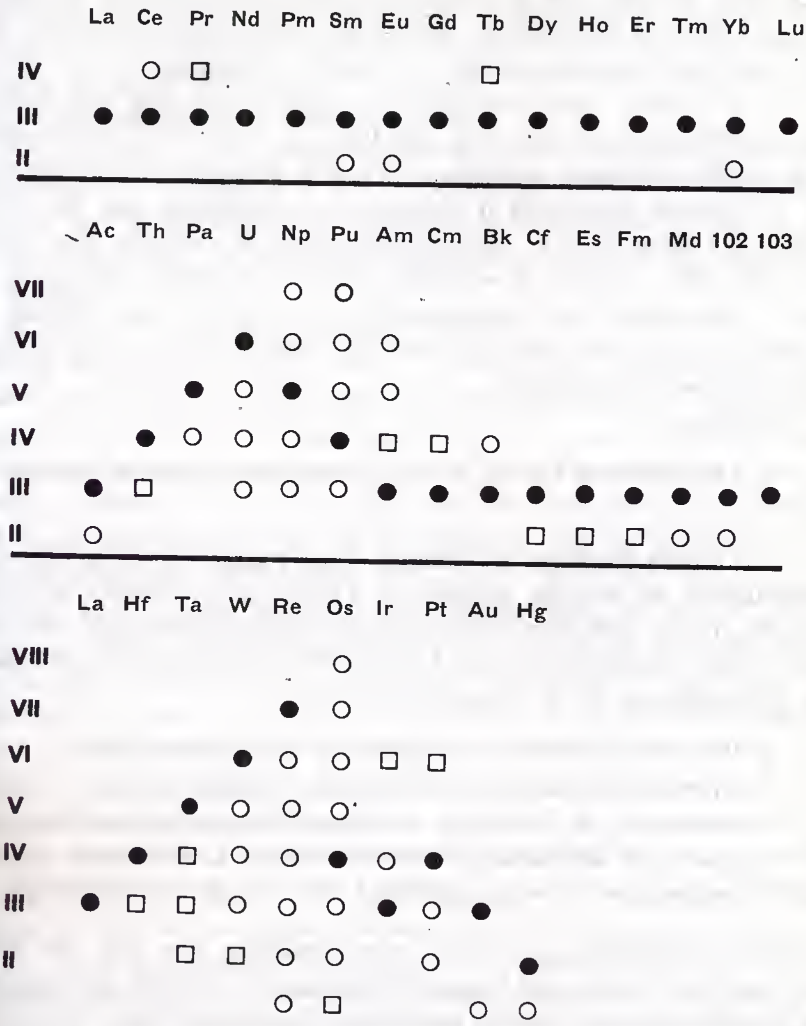


Fig. 1.
États d'oxydation: ● stable, ○ instable, □ à l'état solide seulement.

dation maximal à l'état gazeux avec l'augmentation du nombre atomique, forte tendance à la formation de compexes, phénomènes rédox et de dismutation, densité et multiplicité des formes allotropiques des métaux (six pour le plutonium) etc. A partir du curium cependant, les analogies avec

les lanthanides sont accentuées, les états d'oxydation supérieurs disparaissent essentiellement en faveur de la valence III et les propriétés dans cet état deviennent proches dans les deux séries malgré quelques différences encore notables.

Si donc on veut que le système périodique conserve la signification fondamentale qu'il a eue depuis Mendéléev, c'est-à-dire celle d'une charte qui résume nos connaissances sur la chimie des éléments et qui fait ressortir au maximum leurs analogies en même temps que leur évolution et leurs différences, il n'est pas question d'y introduire artificiellement une anomalie nullement justifiée, à savoir à grouper dans une et même série un mélange hétéroclite d'éléments aussi différents que Ac, Th, Pa, U etc. Cette séquence n'a, chimiquement, rien de commun avec celle de La, Ce, Pr, Nd ... Certes, la septième période, comme il a été prévu bien avant la découverte des transuraniens [15], contient une seconde série de « terres rares », qui n'est cependant pas une répétition de la première, mais a ses propres caractères.

En résumé:

1) Les éléments Th, Pa, et U doivent rester dans les colonnes IV, V et VI.

2) Comme McMillan et Abelson l'ont suggéré après la découverte du neptunium, la nouvelle famille des « terres rares » débute avec l'uranium [16]. Cette série d'*uranides* est caractérisée d'abord par une multiplicité d'états d'oxydation, puis à partir du curium, par la stabilisation et la prédominance de la valence III.

3) *On peut* subdiviser cette série en deux sous-groupes:

— *uranides* proprement dits englobant les éléments de $Z = 92$ à 95;

— et *curides*, de $Z = 97$ à 103, éléments essentiellement trivalents et homologues des lanthanides isoélectroniques. L'américium peut être considéré comme un terme de transition entre les deux sous-groupes [17].

Cette classification est, certes, plus complexe que celle des lanthanides, mais elle correspond à une réalité aussi beaucoup plus complexe, et la simplification du schéma représentatif conduirait dans ce cas à un escamotage ou à une déformation des physionomies chimiques des derniers éléments dans le tableau périodique.

La classification proposée est-elle en contradiction avec la configuration électronique $5f^q$ des éléments de $Z = 91$ à 103? La réponse est certainement non, si l'on considère les différences considérables que le comportement physique des électrons $5f$ présente relativement aux électrons $4f$: retard d'apparition, influence de l'état physique, différences

d'énergie $5f$-$6d$ beaucoup plus petites que $4f$-$5d$, effet de l'environnement etc. Les faits chimiques montrent d'ailleurs très clairement eux-mêmes que si dans la série $4f$ un seul électron est mobile, rarement deux, dans la série $5f$, trois, quatre, peut-être cinq (Pu VII) peuvent être plus ou moins facilement éliminés dans des réactions d'oxydation. Il n'est donc pas étonnant si la dépendance des propriétés chimiques de la structure électronique est très différente dans les deux séries: dans le premier cas, succession d'éléments à variation lente et graduelle des propriétés, dans le second cas, une évolution plus complexe.

En conclusion, nous exprimons notre conviction que le Système Périodique de D. I. Mendéléev sortira vainqueur de la dixième épreuve comme il en est sorti de toutes les précédentes, et que dûment complété, il est capable d'incorporer la nouvelle série d'éléments, sans que sa structure soit altérée.

Il est probable, sans que cela soit déjà prouvé, que les deux derniers éléments actuellement connus, de $Z = 104$ et $105$, et même ceux qui les suivent jusqu'à $Z = 112$, abstraction faite des perspectives réelles de leur production nucléaire, trouvent également leurs places normales dans le système périodique en tant que Eka-Th, Eka-Pa ... Eka-Hg. On peut, en effet, admettre avec Seaborg [18] que les configurations électroniques de $Z = 102$ et $103$ soient $5f^{14}7s^2$ et $5f^{14}6d^17s^2$. La configuration de l'élément 104 serait alors $6d^27s^2$, celle de $Z = 105$ — $6d^37s^2$ etc., jusqu'à $Z = 112$ — $6d^{10}7s^2$. Il n'y a, non plus, aucune raison pour supposer à priori que l'évolution des propriétés chimiques avec la structure électronique n'évolue pas ici approximativement comme dans les périodes précédentes. Une indication en faveur de la tétravalence de $Z = 104$ résulterait des expériences de Zvara et al. [19], selon lesquels la volatilité du chlorure serait proche de celle de $HfCl_4$, un peu inférieure. Notre point de vue justifie cette différence, puisque l'homologue immédiat de l'élément 102 est le thorium, dont le chlorure est moins volatil que $HfCl_4$.

En admettant avec C. K. Jorgensen que le remplissage de la sous-couche $7p$ se poursuive aussi normalement dans les atomes de $Z = 113$ et $114$, nous avons essayé de dégager de l'ensemble de l'évolution des propriétés chimiques et des rayons atomiques et ioniques dans les groupes du tableau périodique, quelques différences qui devraient se manifester dans le comportement chimique de $Z = 114$ relativement à son homologue, le plomb [20]. On sait, en effet, que d'après les calculs théoriques et d'après l'espoir des expérimentateurs nucléaires, on aurait un îlot de stabilité autour de ce nombre atomique qui serait un nombre magique protonique, et des possibilités de produire au laboratoire et, peut-être, même trouver dans la nature quelques nucléides au voisinage de ce nombre

en quantités suffisantes pour être décelés, voire étudiés, en particulier $^{298}114$ qui serait un nucléide à double nombre magique ($N = 184$) (voir, par exemple, [18] et [21]).

Il semble que le caractère alcalino-terreux de Pb II soit encore accentué dans l'éka-plomb qui, en solution alcaline, ne formerait pas d'éka-plombite, mais un hydroxyde basique assez soluble. Son état tétravalent serait moins stable que Pb IV et le potentiel normal du couple 114 IV/114 II serait plus positif que celui de Pb IV/Pb II. La tension de vapeur du métal serait plus élevée que celle de $Pb^{o}$. La sulfate, le chromate et l'iodate seraient moins solubles que les sels correspondants du plomb, le carbonate plus soluble, le sulfure assez soluble dans un excès de sulfure alcalin. Certaines de ces propriétés on été prévues aussi par Seaborg [18].

On sait qu'un autre « îlot de stabilité » a été prévu au voisinage du nombre magique, $Z = 126$. En admettant la réalité future de tels éléments bien éloignés, il serait possible que les deux ou trois premiers termes de la huitième période soient encore homologues chimiques de Fr, Ra et Ac, mais il semble dangereux d'extrapoler plus loin. Après la confusion qui régnait pendant tant d'années au sujet de la série $5f$ et qui n'est pas encore dissipée, il ne me paraît pas possible de prédire si les nouveaux électrons apparaissant dans ces atomes ultra-lourds appartiendraient à la sous-couche $7d$, $6f$ ou $5g$ et surtout quelles seraient les propriétés des éléments correspondants.

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# The Periodic System of D. I. Mendeleev and Problems of Nuclear Chemistry.

The rise of nuclear physics and its speedy development proved to be closely connected with the appearance and development of numerous new fields of chemistry. The relation between nuclear physics and chemistry is not merely the sum of the possibilities of the two sciences: it has furthermore acquired a kind of constructive interference effect. One of the best examples confirming this statement consists in the convergence of nuclear physics and chemistry along the lines laid out by the Mendeleev periodic law.

The discovery of the atomic nucleus by Rutherford and the brilliant research made with X-ray spectra by his disciple Moseley, resulted in the discovery of the physical meaning of the atomic number, $Z$, of a chemical element in the Mendeleev periodic system, namely the value of the positive charge of the atomic nucleus of the element. Niels Bohr applied quantum theory to the planetary model of the atom and made it possible to find some properties of the atomic electrons using quantum numbers. In this way, it was obtained a theoretical explanation of the origin of the periodicity of chemical properties of elements. On the basis of his theory, Niels Bohr arrived at the conclusion that, in the 6th period there must be 32 elements and that element 72, missing at the time, must be an analogue of zirconium and not a rare earth element.

Bohr suggested that this new element should be searched for in zirconium ores. And, indeed, in 1923 hafnium was discovered. The discovery of element 75, rhenium, in 1925 was also based on Bohr's theory applied to the Mendeleev periodic system.

There was another extremely significant advance in the interpretation of the Mendeleev system, namely the use of the exclusion principle sug-

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gested by Pauli in 1925. Fermi-Dirac statistics is based on this very principle, and it is fundamental not only for atomic and molecular structures, but also for the theory of atomic nuclei, the universal weak interaction, metals and semi conductors, superconductivity and superfluidity.

We intend, however, to examine the direct connections between the periodic system of elements, and some questions in nuclear physics.

## Structure of the 8th period of the Mendeleev system.

After the discovery of hafnium and rhenium in the Mendeleev periodic system, within its old limits from hydrogen to uranium, there were 4 empty places left which corresponded to elements 43, 61, 85 and 87 and had not been discovered in nature. The first three of them were produced artificially (in different nuclear reactions). Element 87 (and later element 85) was finally discovered in very small quantities in some branches of the natural series of radioactive elements. The basic data of the first production of these four elements are shown in Table I.

TABLE I.

*The first production of the elements 43, 61, 85, 87.*

| Atomic number $Z$ | Element and its symbol | Manner of production | Year of discovery | Author and country |
|---|---|---|---|---|
| 43 | . . . . . . (Tc) | | 1937 | |
| 61 | . . . . . . (Pm) | | 1947 | |
| 85 | . . . . . . (At) | | 1940 | |
| 87 | . . . . . . (Fr) | | 1934 | |

The radiochemical separation of microscopic quantities of these four elements was wholly based on predictions of their chemical properties from the place they occupied in the Mendeleev periodic system.

The discovery of the trans-uranium elements, which broadened the old boundaries of the system by 13 elements, was mainly due to the key role played by the periodic system. The basic data of the first discovery of trans-uranium elements are given in Table II. But here the determination of the chemical properties of the new elements has proved to be more complicated than in the case of merely filling four holes of the system in its old boundaries. It should be remembered that before the trans-

TABLE II.

*First discovery of Transuranium Elements.*

| Element and its symbol | Way of Obtaining | Year | Authors and country |
|---|---|---|---|
| 93. Neptunium (Np) | $U^{238}$ $(n\gamma)$ $U^{239}$ $\xrightarrow{\beta-}$ $N^{239}$ | 1940 | E. Mc Millan a. P. Abelson (USA) |
| 94. Plutonium (Pu) | $U^{238}$ $(\alpha, 2n)$ $Np^{238}$ $\xrightarrow{\beta-}$ $Pu^{238}$ | 1940 | G. Seaborg, E. Mc Millan et al. (USA) |
| 95. Americium (Am) | $Pu^{239}$ $(n\gamma)$ $Pu^{240}$ $(n\gamma)$ $Pu^{241}$ $\xrightarrow{\beta-}$ $Am^{241}$ | 1944 | G. Seaborg, R. James et al. (USA) |
| 96. Curium (Cm) | $Pu^{239}$ $(\alpha n)$ $Cm^{242}$ | 1944 | G. Seaborg, R. James, A. Ghiorso (USA) |
| 97. Berkelium (Bk) | $Am^{241}$ $(\alpha, 2n)$ $Bk^{243}$ | 1949 | S. Thompson, A. Ghiorso, G. Seaborg (USA) |
| 98. Californium (Cf) | $Cm^{242}$ $(\alpha n)$ $Cf^{245}$ | 1950 | S. Thompson, K. Street et al. (USA) |
| 99. Einsteinium (Es) | $U^{238} + 15n \rightarrow U^{253} \xrightarrow{7\beta-} Es^{253}$ | 1952 | Laboratories of Berkeley, Los-Alamos and Argonne-by the radiochemical separation of products of thermonuclear explosion (USA) |
| 100. Fermium (Fm) | $U^{238} + 17n \rightarrow U^{255} \xrightarrow{8\beta-} Fm^{255}$ | 1952 | |
| 101. Mendeleevium (Md) | $Es^{253}$ $(\alpha n)$ $Md^{256}$ | 1955 | A. Ghiorso, B. Harvey et al. (USA) |
| 102. Nobelium (No) | Bombardment of $Cm^{244}$ by $C^{13}$ -ions | 1957 | Swedish-English-American group |
| | Bombardment of $Pu^{239,241}$ by $O^{16}$-ions | 1957-58 | G. N. Flerov, S. M. Polikanov et al. (USA) |
| | Bombardment of $Cm^{246}$ by $C^{12}$-ions | 1958 | A. Ghiorso, T. Sikkeland et al. (USA) |
| | $U^{238}$ $(Ne^{22}, \gamma n)$ $No^{256}$ | 1963 | E. D. Donets, V. A. Shchegolev, V. A. Ermakov (USSR) |
| 103. Lawrencium (Lr) | Bombardment of $Cf^{249,252}$ by $B^{10,11}$-ions | 1965 | A. Ghiorso, T. Sikkeland et al. (USA) |
| | Bombardment of $Am^{243}$ by $O^{18}$-ions | 1965 | E. D. Donets, V. A. Shchegolev, V. A. Ermakov (USSR) |
| 104. Kurchatovium (Ku) | Bombardment of $Pu^{242}$ by $Ne^{22}$-ions | 1964 | G. N. Flerov, Yu. Z. Oganesyan et al. (USSR) |
| | Bombardment of Cf by C-ions | 1969 | A. Ghiorso et al. (USA) |
| | Bombardment of $Am^{243}$ by $Ne^{22}$-ions | 1967 | G. N. Flerov, V. A. Druin et al. (USSR) |

uranium elements were synthesized, thorium, protactinium and uranium were placed in the 4th, 5th and 6th periods respectively, as analogues of hafnium, tantalum and tungsten. In other words the beginning of the 7th period of the system was believed to have a structure analogous to the 5th and not the 6th period. If the structures of the 7th and 5th periods were completely identical, then the elements 93-104 would be analogues of elements from rhenium ($Z = 75$) to radon ($Z = 86$); i.e. Kurchatovium, Ku, element 104 would have been an inert gas. Even the first research work on chemical properties of neptunium and plutonium have shown their similarity to uranium and not to rhenium and osmium. A hypothesis was made that there may exist a group of uranides, i.e. elements with chemical properties similar to those of uranium. One might guess at the existence of about 14 uranides ($Z = 93 - 106$), if one supposes that the 5f subshell in the 7th period is simply shifted by three places to the right compared with the 4f subshell in the 6th period: thus configuration $6d^4 7s^2$ electrons appears before 5f electrons. However, as early as 1944, it was proved that the most stable state of the newly discovered americium (Am) and especially curium (Cm) was 3-valent; and this led Seaborg to develop his famous concept of actinides. According to this idea, elements from actinium to element 103 are analogs of lanthanum and 14 lanthanides. Objections to the actinide theory are based on the well-known and indisputable facts: the first actinides have mainly the highest valence, so differing considerably from lanthanides (thorium to plutonium).

However there was also some evidence in favour of the actinide hypothesis even before the decisive evidence coming from the chemical analogy of Ku and hafnium, which was established in Dubna.

The evidence came from comparisons between lanthanides and actinides; of adsorption characteristics, solubility, spectra of absorption of visible light, ionic radii, and paramagnetic susceptibilities.

The similarity of the structure of the 7th and 6th periods of the Mendeleev system (with the above reservation) has played a most important role in the discovery and chemical identification of new elements beginning with Am and Cm. The failure of the earlier attempts to discover these two elements was accounted for by the untenability of the original supposition that their chemical properties were close to those of Pu. Therefore attempts (based on this supposition) to oxidize Am and Cm to the 6- valence state failed. The success in the chemical identification of Am, and Cm, and, later, 5 successive elements, came only after use had been made of one of the direct consequences of the chemical similarity of lanthanides (beginning with europium) and actinides (beginning with

americium); namely the complete similarity of their ion-exchange separation (Fig. 1). The determination on this basis of the chemical nature of element 101, originally produced with only 17 atoms, was a kind of record at the time. Seaborg and his colleagues gave the element the name Mendeleevium, and emphasised that the name was a sign of tribute to the great Russian scientist whose periodic system had been a key to the discoveries of new elements for almost a century.

In 1966, chemists at Dubna, with a Czech scientist, Ivo Zvara at the head, scored an even greater success. They managed to determine the chemical nature of the first trans-actinide, element 104 (Ku), which had been found in 1964 in Dubna by a group of Soviet scientists, headed by G. N. Flerov.

Zvara and his colleagues had only 12 atoms of Ku in their first experiments, the half life of the isotope being only 0.3 sec. They used ingenious technique of express entrainment of Ku atoms a mixture of niobium and zirconium chloride vapours, transmitting the mixture through an adsorbent which completely adsorbed lanthanide and actinide clorides. In this way, the Dubna scientists gave a convincing demonstration that the chloride volatility of the new element is similar to hafnium, and not to actinides.

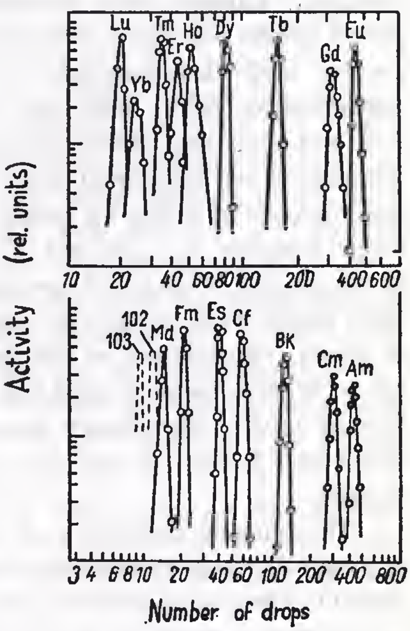


Fig. 1.

Chromatographic curves (Ion-exchange) of lanthanides and actinides separation.

For a long time, it seemed that the question of chemical properties of the elements at the end of the 7th period of the Mendeleev system (to $Z = 118$) was purely academic. In fact, due to the rapidly rising rate of $\alpha$-decay and spontaneous fission with increasing atomic number, the most stable of isotopes of fermium (257 Fm) lives about one billion times less than the longest-lived isotope of plutonium (244 Pu). Extrapolation of similar regularities resulted in the conclusion that, for example, already for element 110, the half life of the longest lived isotope ($^{271}110$) would be only about $10^{-3}$ sec. Thus there would be no question of any study of chemical properties of this element. Having analysed the data obtained later, we arrived at that time [1] at a more optimistic prediction, according

to which the half life of the most stable isotopes of elements (at least up to $Z = 105$ and possibly further) could be measured by days.

Indeed, the neutron excess isotopes, and not the neutron deficient ones, would possess maximum stability (for example, for the element with $Z = 110$, isotopes with mass numbers above 290 (not $^{271}110$). Similar predictions were given by Viola and Seaborg [2] in 1965. Thus there appeared the hope for discovery of some more elements of the 7th period — almost up to the end of the 10th. row of the periodic system. In the literature, three practical ways of effecting the synthesis of these elements were discussed, namely, long bombardment by high neutron fluxes, short period irradiation by superpowerful neutron pulses (under conditions of nuclear and thermonuclear. explosions), and nuclear reactions using multicharged, heavy ions (the way already used to discover elements 102, 103 and 104). Even brighter perspectives for synthesising heavy elements arose after publication of a number of works concerned with the influence of filling up proton and neutron shells located close to the magic numbers $Z = 126$ and $N = 184$. In the same way as the analysis of the periodic changes of chemical properties of elements in the periodic table helped to determine the sequence of the filling of the electron shells in atoms, observations of the periodic character of some of the properties of atomic nuclei formed the foundation for the theory of shell structure of nuclei. The theory was developed mainly by Maria Goeppert-Mayer and Jensen [3] who were awarded the physics Nobel Prize for this in 1960.

The « magic numbers » of protons and neutrons are those values of $Z$ and $N$ which correspond to the complete filling of proton or neutron shells. In the case of electron shells, the « magic numbers » would therefore be the atomic numbers of inert gases — 2, 10, 18, 36, 54, 86, 118. For protons and neutrons the shells are filled in a different way. A greater role is played by the so-called spin-orbit coupling, the proton and neutron energy in the nucleus is strongly dependent on the mutual orientation of their spins and angular momenta. As a result the values of $Z, N = 2$, 8, 20, 50, 82, 126, 184 correspond to filled shells. Except for $N = 184$ and $Z = 126$, 184 all the « magic numbers » are realized among the nuclei already known. As a result of numerous experiments, it was found that nuclei with filled shells have larger binding energies per proton or neutron, and greter resistence to $\alpha$ decay. However, it is spontaneous fission and not $\alpha$ decay that is the most limiting factor for the lifetime of trans-actinides. Therefore the slow $\alpha$ decay of magic isotopes still does not imply the possibility of chemical identification of these elements. Simple estimations based on the drop model enable to find an ap-

proximate relation for spontaneous fission of nuclei with even[2] charge and even[2] mass number:

$$(A = Z + N) \qquad \log. T_{\frac{1}{2}}\,(\text{sec.}) = 157 - 3.75\,\frac{Z^2}{A}$$

which means practically prompt fission (half life $T_{\frac{1}{2}} = 10^{-12}$ sec.) for $\frac{Z^2}{A} = 45$, and limited possibility for chemical study of new elements somewhere about $Z = 110$. In view of this, some conclusions made in 1965 by Myers and Swiatecki [4] and confirmed later by others (we would like to single out calculations made by V. Strutinsky and Y. Musychka [5]) appear to be important. These observations showed (table between pp. 162 and 163) that it was possible to obtain greater stability of nuclei with respect to spontaneous fission as the magic numbers $Z = 126$ and $N = 184$ are approached. Fig. 2 based on these estimates shows the area of relatively stable isotopes which may be studied by both physical and chemical means. All isotopes stable to the emission of neutrons (lower limit) or protons (the upper limit is the line where the energy for proton emission exceeds 3 MeV) are marked with dots. The darkened area of isotopes already known is less than 30% of the total area of potential radioactive isotopes having one of the 5 main types of decay: $\alpha$ decay, $\beta$ decay ($\beta^-\beta^+$ decay, electron capture) spontaneous fission, proton-decay, two proton-decay.

In the absence of the shell effects which make nuclei around $N = 184$ (especially close to $Z = 126$) more stable, the upper limit of stability (to spontaneous fission) for the heaviest isotopes would be a sort of horizontal line.

The higher barrier to fission from shell effects results (according to calculations) in the appearance of the «isthmus of stability» which is shown by a step line, and which widens most in the vicinity of $Z = 126$.

According to some theoreticians, the filling of shells near $Z = 82$-$126$ might result in a widened isthmus of stability also near $Z = 114$.

The following are examples of nuclear reactions which can be carried out on an accelerator of heavy multicharged ions and which lead to the formation of «doubly magic» nuclei $Z = 126$, $N = 184$

$$^{242}_{94}Pu_{148} + {}^{72}_{32}Ge_{40} \rightarrow 4n + {}^{310}126_{184}$$

$$^{232}_{90}Th_{142} + {}^{82}_{36}Kr_{46} \rightarrow 4n + {}^{310}126_{184}\,.$$

Other nuclei, e.g. $^{298}114_{184}$, can be produced by acceleration of nuclei of the heaviest natural elements — uranium for instance. The fusion of two

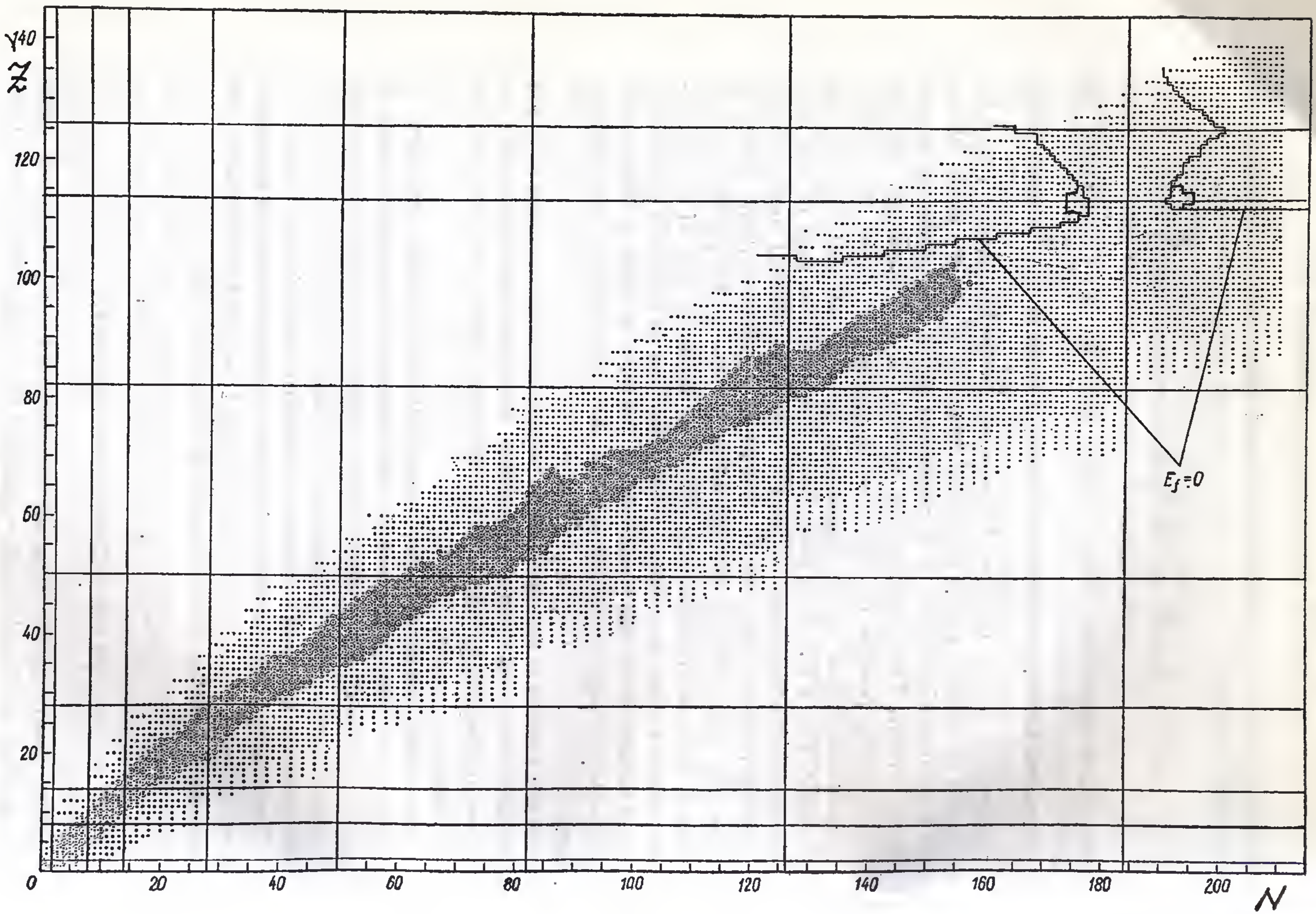


Fig. 2.

such nuclei must lead to fission, and this isotope may be produced in the fragments; for example

$$^{238}_{92}U_{146} + {}^{238}_{92}U_{146} \rightarrow {}^{476}184_{292}$$

$$\rightarrow {}^{298}114_{184} + {}^{166}_{70}Yb_{96} + 12n$$

Apart from this, according to a very interesting conjecture by G. N. Flerov, some isotopes of element 114 (eka lead) are sufficiently long lived to be found in nature in the form of micro-impurities of lead (recognized, for instance, by tracks of fragments from spontaneous fission of isotopes of element 114 in old lead glasses). Thus there is a real possibility of obtaining stable isotopes, in the isthmus of stability, of a great many trans-actinide elements and studying their chemical properties. In this connection, the problem of the structure of the 8th period of the Mendeleev system becomes important. It is generally assumed in the literature (e.g. [6, 7]) that structure of this period would be similar to the preceding two, i.e. the period would contain 14 eka-actinides, namely elements 122 to 135. Then element 126 should be a chemical analogue to Pu, and elements 122-126 should have a valence higher than three. We think [8], however, that the 8th period of the Mendeleev system must contain 50 elements and not 32 (from 119 to 168) in which electron shells $8s^2$, $p^6$, $7d^{10}$, $6f^{14}$, $5g^{18}$ are filled in sequence discussed below. In this case, elements from 139 to 153 should be analogues of actinium. Furthermore, actinides, and all elements near the magic value $Z = 126$, must represent a newly appearing group of « octadecanides », namely 18 elements in whose atoms the 5g electron shell is being filled ($Z = 121$-$138$). For all octadecanides the most stable valence is three, and the nearest analogue is actinium (just as ittrium bears a similar relation to lanthanum and the lanthanides). One would expect that octadecanides will differ from each other even less in their chemical properties than in the case of rare-earth elements.

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Fig. 2. — *Stable and radioactive isotopes:*

$Z$ - number of protons in nucleus, equal to element number in the periodic system;

$N$ - number of neutrons in nucleus.

Nuclei with odd number of protons or neutrons are somewhat more stable to fission and their half-lives are longer by several orders of magnitude than for even-even nuclei.

The darkened area shows isotopes already known. The upper limit is determined by the predicted instability to the emission of protons (energy of proton binding is $\beta_p < (-3)$MeV), the lower limit by the predicted instability to the emission of neutrons (energy of neutron binding is $\beta_n < 0$). In the top right hand corner you can see a possible isthmus of stability to spontaneous fission in the neighbourhood of $N = 184$, $Z = 126$ and $Z = 114$. In the absence of the shell effects spontaneous fission would lead to the limiting line of stability in the form of a horizontal line somewhere about $Z \approx 110$-$112$.

However, it may still not be possible to synthesize these elements and study their chemical properties. This applies even more to the 50 elements of the 9th period of the Mendeleev system ($Z = 169$-$218$), which, in principle must be quite analogous to the 8th period.

Arguments for the supposed structure of the 8th period of the Mendeleev system, and the analysis of the sequence of filling electron shells, can be given within the theory of sequence of filling of $(n + l)$ groups developed by V. M. Klechkovskii [9-11]. According to his rule, originally presented [9] as empirical, the filling of electron shells procedes with increasing values of $(n + l)$: $(n + l) = K = 1, 2, 3, \dots$ With each given value of $K$, the process of filling goes from large « $l$ » and small « $n$ » to small « $l$ » and large « $n$ » ([1]), i.e. (taking into account the condition $l \leq n - 1$) in the sequence:

$$\left.\begin{aligned} l &= \frac{K-1}{2}\,;\ \frac{K-3}{2}\,;\ \dots\,;\ 0 \\ n &= \frac{K+1}{2}\,;\ \frac{K+3}{2}\,;\ \dots\,;\ K \end{aligned}\right\}\ \text{for odd K}$$

$$\left.\begin{aligned} l &= \frac{K}{2} - 1\,;\ \frac{K}{2} - 2\,;\ \dots\,;\ 0 \\ n &= \frac{K}{2} + 1\,;\ \frac{K}{2} + 2\,;\ \dots\,;\ K \end{aligned}\right\}\ \text{for even } K\,.$$

It can easily be seen that the number of elements with a given value of $n + l = K$ is $\frac{(K+1)^2}{2}$ for odd $K$ and $\frac{K^2}{2}$ for even $K$. To describe the type of electron configuration of atoms on the basis of the $n + l$ sequence, V. M. Klechkovskii introduces the parameter $\varepsilon_K$ which he calls the configuration index [10] and which is equal to the sum of the number of vacancies in all $nl$ states for a given value of $n + l$. Thus, as states

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([1]) However, in element 121, $6f$ or $7d$ electrons may appear, and not $5g$. There are similar exceptions to the Klechkovskii rule for La (appearance of $5d$) and Ac (appearance of $6d$), but later, for $Z > 122$ (octadecanised), the $5g$ shell will be filled, ending with $Z = 138$. It should be pointed out that when G. T. Seaborg [6] analysed elements 122-126 as analogues of Th-Pu (without taking into account $5g$ electrons), he had previously emphasized the possibility of the appearance of $5g$ electrons in that area [12]. Inded, very simple calculations on the basis of the Thomas-Fermi model showed that the $5g$ subshell begin at $Z = 113$ for the parameter $a = 0.155$ [13] (here $Z_l = a\,(2l + 1)^3$) and at $Z = 124$ for $a = 0.170$. The latter value of $a$ was found theoretically [14] and is compatible with the data on $d$ and $f$ electrons.

with odd $K$ are being filled there is a decrease in $\mathcal{E}_K$ from $\frac{(K+1)^2}{2}$ to 0, and then an increase to $\mathcal{E}_K = \frac{(K+1)^2}{2} - 1$. As states with even $K$ are being filled, the value of $\mathcal{E}_K$ decreases from $\frac{K^2}{2} - 1$ to 0, after which there is an increase to $\frac{(K+2)^2}{2} - 1$. Evidently, as shells with different $(n+l)$ are filled, the values of $Z$ become

| $(n+l) = K$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| $Z$ | 2 | 4 | 12 | 20 | 38 | 56 | 88 | 120 | 170 |
| $(\mathcal{E}_K)_{\max}$ | 1 | 1 | 7 | 7 | 17 | 17 | 31 | 31 | 49. |

In his papers [10, 11] V. M. Klechkovskii showed that the above $(n+l)$ sequence rule can be deduced theoretically on the basis of the Thomas-Fermi statistical model. Limits, within which all levels with a given $n+l$ are filled, are described as follows:

$$\left\{\frac{1}{6}(n+l)^3 + (n+l)\cdot\left[\frac{1}{2}\cos^2\frac{\pi}{2}(n+l) - \frac{1}{2}\right]\right\} \leq Z \leq$$

$$\leq \left\{\frac{1}{6}(n+l+1)^3 + (n+l+1)\cdot\left[\frac{1}{2}\sin^2\frac{\pi}{2}(n+l) - \frac{1}{6}\right]\right\}.$$

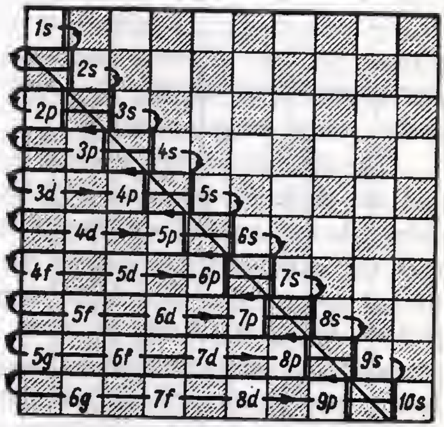


Fig. 3.
Scheme of the successive filling of the shells.

Elements of different periods which are chemical analogues are characterized by the same configuration index $\mathcal{E}_K$ (except for gelium, for which $\mathcal{E}_K = 0$ and not 2 as for the other inert gases).

Fig. 3 is a graphic illustration of the Klechkovskii rule Filling up of shells proceeds in the sequence shown by the curved dashed line, and the boundaries between the periods of Mendeleev system are shown by a diagonal going from top left to bottom right of the figure. A similar illustration of the sequence of filling of electron shells is given with the help of a 64 cell «chess board» in [15]. With the 8th and 9th periods included, it will be necessary to resort to a 100 cell chess board.

Applying the $(n + l)$ sequence rule to the end of the 7th and 8th periods of the M. system we arrived at the framed structure of the 8th period:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $n + l = K$ | 8 | 8 | 8 | 8 | 9 | 9 | 9 | 9 | 9 |
| $n$ | 5 | 6 | 7 | 8 | 5 | 6 | 7 | 8 | 9 |
| $l$ | 3 | 2 | 1 | 0 | 4 | 3 | 2 | 1 | 0 |
| $nl$ | $5f$ | $6d$ | $7p$ | $8s$ | $5g$ | $6f$ | $7d$ | $8p$ | $9s$ |
| Elements | 89—102 | 103—112 | 113—118 | 119—120 | 121—138 | 139—152 | 153—162 | 163—168 | 169—170 |

Fig. 4 shows all the Mendeleev table, where we have singled out 18 « *g*-shell » elements of the 8th and 9th periods (octadecanides); 14 « *f*-shell » elements of the 6th, 7th, 8th and 9th periods; and « inserted decades » of « *d*-shell » elements of the 4th-9th periods ([2]). The $(n + l)$ sequence rule is occasionally not completely satisfied in the order of filling of $5d$ and $4f$ shells in the lanthanides and in $6d$ and $5f$ shells in the actinides (this in especially significant from thorium to Np). It can, however, be clearly seen from the table that « *f*-shell » elements of the 6th and 7th periods join the electron analogues of scandium and yttrium (lutecium and lawrencium), having $\mathcal{E}_K = 17$, a configuration $ns^2(n - 1)d$ of outer shells, and a main valence of 3.

The stability of this valence is characteristic for lanthanum, actinium and eka-actinium (element 139) and is also expected for the octadecanides (the 18 « *g*-shell » elements of the 8th period). One might expect that the octadecanides will be close in their chemical properties to actinium and further that these properties will not be influenced by competitive filling of $7d$ and $6f$ states. This competitive filling could lead to prevalence of valences greater than 3, as is the case with the first actinides. In this way, the laws of the periodic system, upon application to the eighth period allow prediction of not the analogy, but on the contrary, of certain differences of the new 8th period from all the other periods already known. Therefore, synthesis of elements of the 8th period and a study of their physical and chemical properties must be of great interest not only for nuclear physics, but also for general and inorganic chemistry.

There is hope that successful experiments on accelerators of heavy multicharged ions will lead in the coming years to synthesis and study of the chemical properties of the far trans-actinide elements in the region of the isthmus of stability, throwing light on the structure of the 8th period of the Mendeleev system.

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([2]) Helium is placed on the extreme right hand column of the table with configuration index $\mathcal{E}_K = 2$, together with the other incert gases. However, according to the value of $\mathcal{E}_K$ mentioned above, it must be in the 2nd column, above Be.

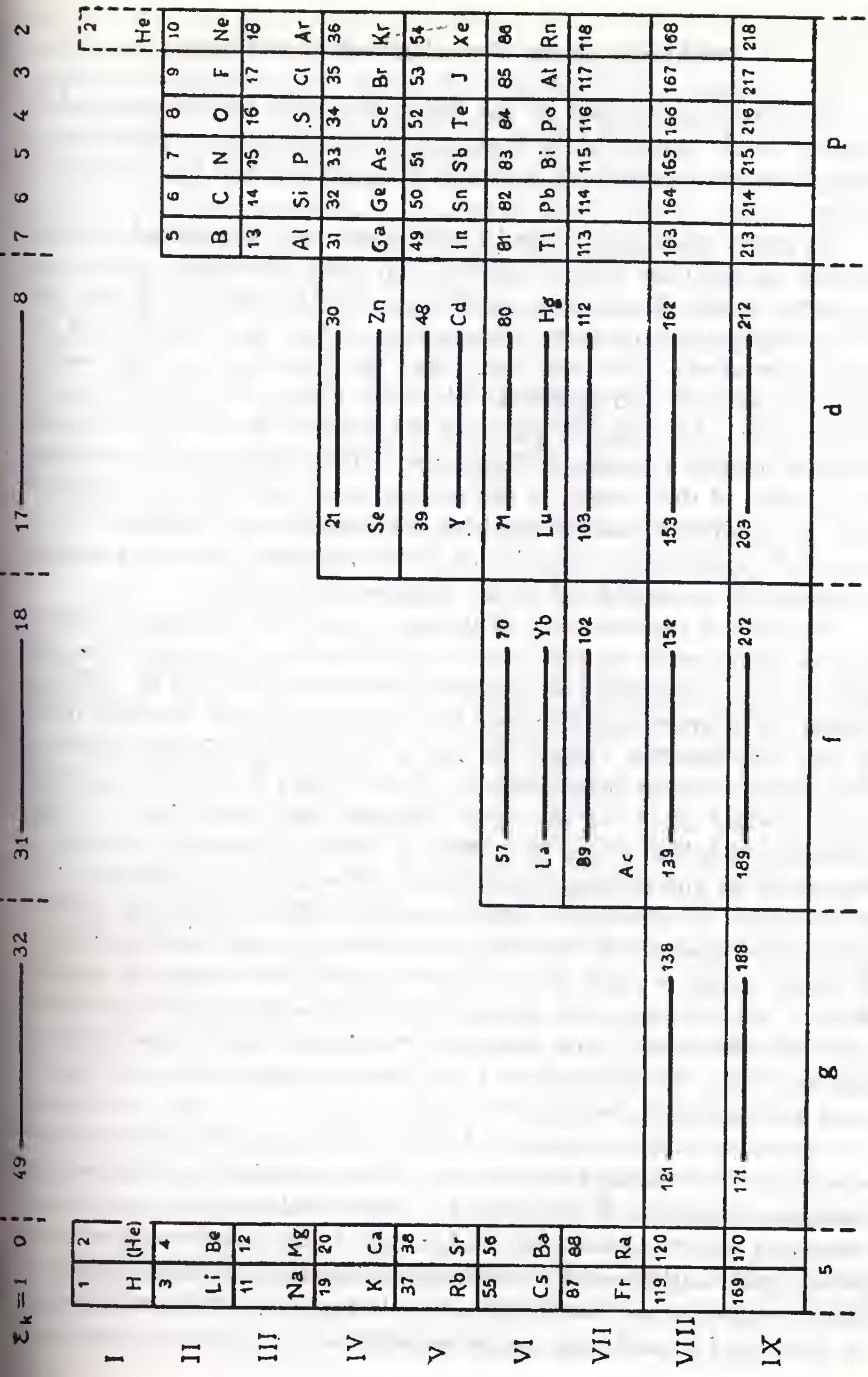


Fig. 4.

The periodic system of D. I. Mendeleev, including the eight and ninth periods.

## Problems of the Chemistry of New Atoms.

All atoms represented in the Mendeleev table are characterised by equality in the nature of their electric charge carriers: protons have a positive charge concentrated in the nucleus and electrons have a negative charge.

In recent years the so-called « new atoms » were discovered, in which protons or electrons were substituted by other elementary particles of the same charge. Elementary particles are now counted by dozens. Different combinations of these particles can, in fact, give hundreds of different new atoms. Does this mean that the Mendeleev periodic system must be extended and modified? We think it does not. Substitution of electrons by other negative particles (for instance, by $\mu^-$ or $\pi^-$ mesons) does not involve a change in the charge of the nucleus which determines the position of the element in the periodic table. Substitution of protons by other positively charged particles, for example by a positron ($e^+$) or muon ($\mu^+$), leads to the formation of atoms which can, as far as chemistry is concerned, be considered to be isotopes of hydrogen.

Analysis of the chemistry of the new atoms can be begun with such peculiar members of the first square of the Mendeleev periodic table such as the Ps atom, consisting of a positron and an electron, and the Mu-atom formed by a muon and electron. Ps, discovered by M. Deutsch (USA) in 1951, was the first example of the new atoms, and is the lightest of all (920 times lighter than hydrogen). Both Ps and Mu can be considered to be labelled atoms of hydrogen, although they differ from ordinary radioactive labelled atoms in having a lifetime and decay mechanism dependent on the chemical environment. The maximum lifetime of Ps in its triplet or ortho-state, ${}^{T}Ps({}^{3}S_1)$ with parallel electron and positron spins, in the absence of any chemical reactions (i.e. the intrinsic lifetime of Ps in vacuo) is equal to $1.4 \times 10^{-7}$ seconds. For singlet or para-Ps, ${}^{s}Ps({}^{1}S_0)$, with electron and positron spins anti-parallel, the intrinsic lifetime is still shorter, only $1.25 \times 10^{-10}$ seconds. The lifetime of Mu is determined by the decay rate of the muon ($\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$) and is equal to $2.2 \times 10^{-6}$ seconds.

The short intrinsic lifetime of Mu, and especially Ps, may be used as a convenient standard in the study of fast chemical reactions of such hydrogen-like atoms. It helps one to observe and study the role of diffusion and quantum effects in the kinetics of such reactions. Because of the negligible half life of Ps and Mu their steady-state concentrations in ordinary experiments, when radioactive isotopes (e.g. ${}^{64}Cu$ or ${}^{22}Na$) are the sources of $e^+$ and high energy accelerators of $\mu^+$, do in general not

exceed a few atoms per cubic centimetre. There can be no question of any chemical methods of observing transformations of these atoms. Research into the chemistry of Ps and Mu is done by radio-technical methods of contemporary nuclear and elementary particle physics. They allow one to follow the fate of each single atom of Ps and Mu.

Among the characteristics of positron annihilation which change, together with the chemical and crystalline state of the material, is the positron lifetime (i.e. the interval from the moment the positron gets into the material to its annihilation), the number of $\gamma$-quanta emitted upon the annihilation, and the angle between the direction of two quanta.

There exist three main mechanisms of positron annihilation:

1) free collisions with the outer valence shell electrons of atoms and molecules (the inner shells are less accessible owing to the Coulomb repulsion of the positron by the nucleus) and with conduction electrons in metals;

2) by formation of Ps (with probability 3/4 in the form of $^{T}$Ps and 1/4 in the form of $^{S}$Ps);

3) by formation of bound states with a neutral molecular fragments ($e^{+}M$) or with anions ($e^{+}A^{-}$).

Each of these mechanisms leads to specific features of the annihilation. In the cases of free collisions or formation of bound states or para-Ps, two photons are emitted and the annihilation is characterized by the shortest lifetime of the positrons in the material. Formation of ortho-Ps results in a longer half lifetime, up to $10^{-7}$ secs. in gases and $10^{-9}$ secs. in the condensed phase. If the positron annihilates with an electron in the ortho-Ps state, three photons are emitted. However, if ortho-Ps undergoes the reactions given below, i.e. quenching occurs, only two photons are emitted (as in the examples above). Finally, if annihilation proceeds from para-Ps, the angle between the two photons is only 0.5 m.rad. from 180° (due to thermal movement of the Ps atoms). In the case of annihilation of positrons on valence electrons or on conduction electrons, the deviation of the angle between the two photons from 180° is several milliradians. Thus, para-Ps is responsible for the so-called « narrow » component and the other modes for the wide component of the angular correlation of the photons. From the above discussion, we see that the experimental methods of observation of positron annihilation consist of detecting the number of $3\gamma$ coincidences (from ortho-Ps), (Fig. 5*a*) observation of delayed coincidences between the times of positron creation and annihilation (Fig. 5*b*), and in observation of the dependence of $2\gamma$ coincidences rate on the angle between two gammas (Fig. 5*c*).

As a result of combining the above methods, it is possible to study the influence of chemical environment on the probability of Ps formation, and thus the different mechanisms of Ps inhibition and the duration of its lifetime which is reduced by different reactions of quenching of ortho-Ps. One of these quenching reactions is the so-called « pick-off » annihilation (on « strange » electrons at the moment of collision of a Ps atom

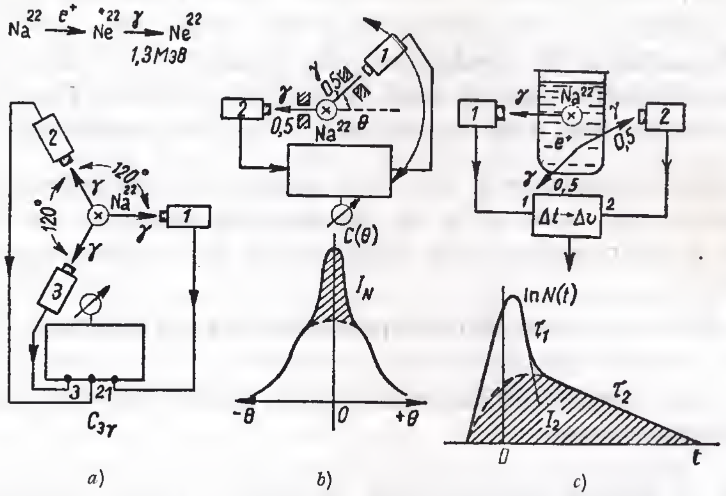


Fig. 5.

Schemes of the main experimental methods of investigating positron annihilation

*a*) Counting of triple coincidences $C_{3\gamma}$

*b*) Angular correlations of the annihilation quanta; the counting rate $C_\gamma(\theta)$ as a function of the angle between two quanta $(\pi - \theta)$. $I_N$ = « narrow component » (shaded area).

*c*) Observation of the positron lifetime. $N(t)$ is the number of annihilation events in the time interval from $t$ to $t + \Delta t$, where $t$ is counted from the moment of emission of the positron, which is detected by the 1.3 Mev cascade quantum of the $^{22}$Na decay (see top-left). $\Delta t \to \Delta v$ means the device which transforms the delay time of the incoming signals of counter 2 relative to counter 1, into the amplitude. $\tau_1(\tau_2)$ is the short (long) lifetime; $I_2$ is the intensity of the long-lived component; 1, 2, 3 are the scintillation counters.

and molecule), ortho-para conversion (conversion of ortho into para-Ps in interactions with paramagnetic centres), and all possible chemical reactions of Ps where it behaves as a hydrogen-like atom.

In recent years, various quenching reactions, both in the condensed and gaseous phases, were studied at the Institute of Chemical Physics of the Academy of Sciences of the USSR by means of all the above experimental methods [16, 17]. We give below some examples of such reactions

| | |
|---|---|
| substitution: | $Ps + Cl_2 \rightarrow PsCl + Cl$ |
| addition: | $Ps + (CF_3)_2NO \rightarrow (CF_3)_2NO\ Ps$ |
| oxidation: | $Ps + Fe^{3+} \rightarrow e^+ + Fe^{2+}$. |

A brief summary of the results and trends of our theoretical and experimental study of the physical chemistry of the positron and Ps are given in Table III. Comparison of rate constants and various Ps and hydrogen atom reactions of a general character lead to the conclusion that, though they have common chemical properties, there are some differences. These are caused by the considerable difference in mass — it has already been mentioned that the Ps atom is 920 times lighter than hydrogen, while the heaviest atom known at present is only 260 times heavier. Fig. 6 is a schematic illustration of the above statements.

What effects does this difference in masses lead to? First of all, it leads to quite peculiar features of molecules where a hydrogen atom has been replaced by a Ps atom. Consider, for example, an $H_2$ molecule — it is a typical two-center molecule —, where two electrons move in the field of two almost immovable protons. When the replacement is made to form a molecule of HPs, we now have a single centre molecule, where the two electrons and positron form a peculiar electron-positron shell. In other words, the only nucleus is surrounded by a cloud of two electrons and a positron. This «molecule» rather reminds the three electron lithium atom. If positronium is considered, from a qualitative point of view, as one entity within a molecule, one might presume that, owing to its small mass, the zero-point vibration frequencies will be much higher than for hydrogen. Accordingly, the dissociation energies of molecules like PsM will be less than those of similar molecules, HM. Therefore, all chemical bonds of Ps atoms should be considerably weaker than those of hydrogen, and all reactions replacing H-atom by Ps should be endothermic. Moreover, reactions of substitution and addition which, are exothermic for hydrogen, will, as a rule, be less so and in many cases even endothermic for Ps. On the other hand, as the Ps ionization potential ($\sim$ 6.8 eV) is half of that of hydrogen, oxidation reactions of Ps in the gaseous phase must be easier by about 6.8 eV than the corresponding oxidation of hydrogen. However, in water solutions, the picture may again be different as the energy of hydration of $H^+$ ($\sim$ 11 eV) is much higher than that of $e^+$ (1-2 eV).

Apart from energetic differences there are kinetic ones in the behaviour of Ps as compared to hydrogen, again caused by the small mass of Ps. For example, the energy dependence of the cross sections for endothermic reactions of substitution with participation of Ps, as in $Ps + Cl_2 \rightarrow PsCl + Cl$, reminds one of dissociative capture of an electron, $e^- + Cl_2 \rightarrow Cl^- + Cl$, and not of reactions with hydrogen atoms. As in the case of electron capture, the cross section for substitution of a heavy atom by Ps attains its maximum value near threshold and then drops rapidly in an interval of energy equal to that of the vibrational energy

### Table III.

*Examples of Theoretical Studies of Physical Chemistry of Positron and Positronium.*

| Theory of Resonance (via $e^+M$) | Theory of Single-Center Molecules (e.g. $e^+H^- \equiv PsH$) | Theory of $e^+$-Polaron states and its bonds with lattice defects | Theory of Reactions of Substitution of Ps: $Ps + M_1M_2 \rightarrow PsM_1 + M_2$ |
|---|---|---|---|

*Examples of Experimental Studies*

| Reaction | Method | Result |
|---|---|---|
| $e^+C_6H_6 \rightarrow Ps + C_6H_5^+$<br>$e^+C_6H_5I \rightarrow C_6H_5Ie^+$ | $\tau_2 I_2$ | Demonstration of new way of definition of rate-constants of $e^+$-and $e^-$ elementary processes |
| $Ps + Ox \rightarrow e^+ + Red$ | $c_{3\gamma}$ | Quenchig of PS is a kinematical effect, not determined by the Red-Ox Potential |
| $\left[\begin{array}{l} Ps + Fe^{3+} \rightarrow e^+ + Fe^{2+} \\ Ps + Fe^{2+} \rightarrow [PsFe^{2+}] \end{array}\right.$ | $\tau_2 I_2$ | Far Tunneling does not play a decisive Role in Oxidation (Comparison of PS and H Reactions) |
| $\left[\begin{array}{l} \text{ortho-}Ps + Mn^{2+} \rightarrow \text{para-}Ps + Mn^{2+} \\ Ps + MnD'_4 \rightarrow \text{oxidation} \end{array}\right]$ | $\tau_2 I_2$<br>$\vartheta_{2\gamma}$ | Separation of Conversion and Oxidation by Methods |
| ortho-Ps + $Co^{2+} \rightarrow$ para-Ps + $Co^{2+}$ ($CoCl_2$ in weter, alcohols and their mixtures) | $\tau_2 I_2$ | PS is extremely sensitive to the structure of coordination sphere around the ion and to the delocalization of $e^-$ |
| Ps + DPPH and other free radicals ($\eta$ changed by $t^o$ and by composition of solvent) | $\tau_2 I_2$ | New Method of separation of kinetical and Diffusional Parameters for Reactions in Solutions |
| ortho-Ps + NO $\leftarrow$ para-Ps + NO | $\vartheta_{2\gamma}$ | PS can be used as a detector of free radicals in gases |
| $Ps + Cl \rightarrow PsCl + Cl$ | $\vartheta_{2\gamma}$ | PS-M binding energy can be determined from kinetical data |
| $\text{ortho-}Ps + NO_2 + N_2O_4 \begin{array}{l} \nearrow \text{para-}Ps \\ \searrow PsNO_2 + NO_2 \end{array}$ | $\vartheta_{2\gamma}$ | Demonstration of the possibility of PS-methods of detection of rates of fast reactions and τl.fe (< $10^{-12}$ sec) of intermed |

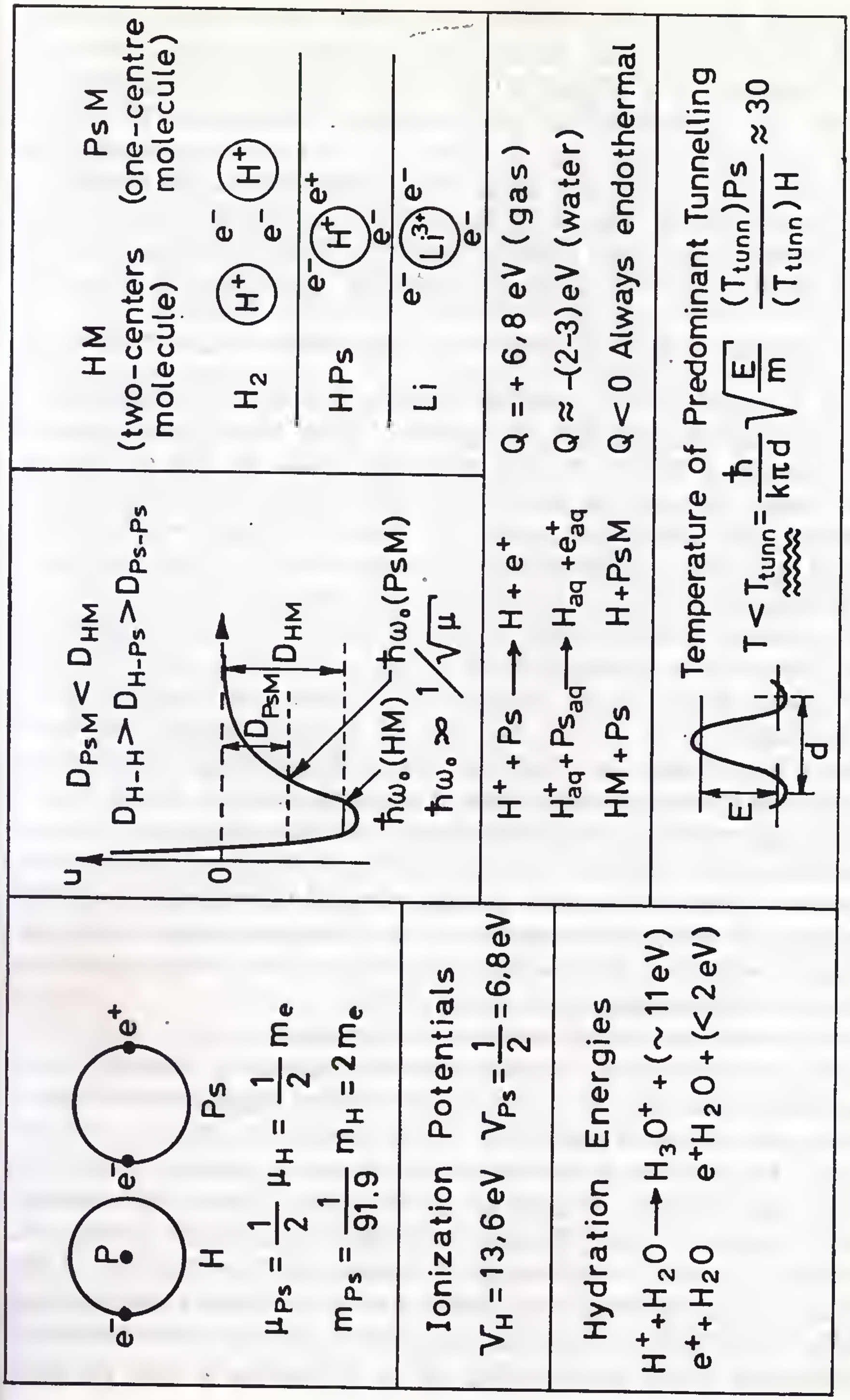
e⁻ P H e⁻ e⁺ Ps
μPs = 1/2 μH = 1/2 me
mPs = 1/91.9 mH = 2 me
Ionization Potentials
VH = 13,6 eV VPs = 1/2 = 6,8 eV
Hydration Energies
H⁺ + H2O ⟶ H3O⁺ + (~ 11 eV)
e⁺ + H2O e⁺H2O + (< 2 eV)
DPsM < DHM
DH-H > DH-Ps > DPs-Ps
u
0
DPsM
DHM
ħω₀ (HM)
ħω₀ (PsM)
ħω₀ ∝ 1/√μ
HM (two-centers molecule)
PsM (one-centre molecule)
H2 H⁺ e⁻ e⁻ H⁺
HPs e⁻ H⁺ e⁻ e⁺
Li e⁻ Li³⁺ e⁻ e⁻ e⁻
H⁺ + Ps ⟶ H + e⁺ Q = + 6,8 eV (gas)
H⁺aq + Psaq ⟶ Haq + e⁺aq Q ≈ -(2-3) eV (water)
HM + Ps H + PsM Q < 0 Always endothermal
E
d
Temperature of Predominant Tunnelling
T < Ttunn = ħ/(kπd) √(E/m)
(Ttunn)Ps / (Ttunn)H ≈ 30

Fig. 6.

level of the initial molecule. Thus, transitions of an electron between a Ps atom and another one should not be considered as adiabatic, i.e. as unaccompanied by a change in the distance between the positron and nucleus. The pre-exponential factor in gaseous reactions of Ps must be thirty times larger than that for hydrogen. Even more important is the fact that a free, non-solvated, atom of Ps can effectively act in the reaction by means of tunnel penetration through the potential activation barrier. The « tunnel temperature », below which the tunnel effect predominates exponentially over the ordinary. Arrhenius mechanism of interaction is proportional to $\left(\frac{E}{d^2m}\right)^{\frac{1}{2}}$, where $d$ is the barrier width, $E$ its height and $m$ the mass of the tunnelling particle. For Ps, this temperature is very much higher than that for hydrogen. Thus, when Ps and hydrogen are compared according to their properties which are due to their nuclear charge, they should occupy the same place in the periodic table. However, their differences caused by mass, or atomic weight, clearly emerge in the spirit of Mendeleev's original approach to the periodisation of chemical properties. All this is of specific interest in studying the physical chemistry of the positron and Ps, in particular the connection between this problem and the periodic system of elements. Apart from this, as has been shown by the research carried out at the Institute of Chemical Physics of the USSR Academy of Sciences, various transformations of Ps can serve as a basis for observation of delocalization of spin density and change in accessibility of unpaired electrons due to the formation and rearrangement of complexes with para magnetic centers (in solutions), for development of new methods of detection of free radicals (especially in gases), the study of mechanism of triplet-singlet transitions (especially in solids), determination of the lifetimes of short lived intermediate complexes PsM* ($\sim 10^{-12}$ secs) in gases, and, finally, elucidation of the role of tunnelling in chemical kinetics.

In recent years, much work on Mu chemistry has been done at the Institute of Theoretical and Esperimental Physics in Moscow [17-19]. Experiments with Mu are based on the study of angular distributions of positrons in decays of $\mu^+$ relative to the original direction of motion of the $\mu^+$. The $\mu^+$-mesons are formed in the weak process$\pi^+ \rightarrow \mu^+ + \nu_\mu$ and become polarized because of parity violation, their spins oriented mainly opposite to their direction of motion. A successive decay, $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$ is also a weak interaction process and, therefore, the number of positrons moving in the same direction as the $\mu^+$ must be less than those moving in the opposite direction. Repeated formation and disintegration of Mu atoms causes depolarization of the $\mu^+$ mesons so that the direc-

tional distribution of the positrons is smeared out. But as soon as the Mu atom undergoes a chemical reaction and forms diamagnetic MuM, depolarisation of the $\mu^+$ stops. Thus, the sooner the Mu reacts, the stronger is the anisotropy of the emerging positrons relative to the axis of the $\mu^+$ beam.

The sample to be studied is bombarded by a beam of $\mu^+$ mesons, and is usually placed in a transverse magnetic field so that the rotation angle of the positron counters does not change. Due to precession of spin in the magnetic field, the angle between its direction and the fixed direction of motion of the decay positron changes periodically with time. Polarization of the meson causes corresponding periods in the count of the decay positrons, which is illustrated in Fig. 6. (Experiments with $\mu^+$ mesons at rest in $CHBr_3$; precession curves are corrected for the number of mesons decreasing with time as a result of their decay). The frequency of spin precession for a free triplet Mu atom (here this frequency is approximately 100 times larger than for a $\mu^+$-meson, because the spin value is 2 times and the magnetic moment ca. 200 times greater), and for a free $\mu^+$-meson differs greatly. If Mu undergoes a chemical reaction forming an ordinary two- electron bond, the precession frequency turns out to be like the $\mu^+$ because of compensation of spins of the two electrons. (This particular example is given in Fig. 6). If, on the other hand, the Mu atom is doubly bonded to produce a radical, than there is no precession with $\mu^+$-meson frequency. All this makes it possible not only to determine the total rate constant of the Mu atom reactions (for example with $C_6H_5Hal$ molecules), but also to separate the contributions of substitution reactions with formation of molecular products like MuH or MuHal, and radical products like $C_6H_5HalMu$ [19]. By using the results of experiments with Mu it is possible to determine a number of rate constants for hydrogen reactions with greater precision than in direct experiments on hydrogen.

Energies of Mu bonds with various atoms must be smaller than those of hydrogen, and therefore substitution reactions $Mu + HM \rightarrow H + MuM$ will be, as a rule, endothermic, though less so than with Ps. The ionisation potential of Mu (as well as its radius) coincides with that of hydrogen to within 0.5% and so we do not expect great differences in the energies of gaseous state oxidation of H and Mu. In comparing the oxidation data in solutions, however, it is necessary to remember that the hydration energy of $\mu^+$ is probably considerably less than that of $H^+$. The mass of the $\mu^+$ is large enough so that molecules formed by Mu and various atoms may be considered to be two-centre ones, and transitions of an electron from $\mu^+$ to another nucleus as proceeding without a change in distance between the nuclei. The « tunnelling temperature » in Mu reactions must be about three times higher than that for hydrogen and

5-10 times lower than for Ps. Thus, Mu occupies a position between Ps and hydrogen, and the study of Mu reactions is of interest for all the above reasons (in particular, in connections with the dependence of chemical properties on the mass of the atom).

Unexpected connections of nuclear chemistry with the Mendeleev periodic system were discovered by a group of scientists of the Nuclear Problem Laboratory of the Joint Institute for Nuclear Research while studying the capture of $\mu^-$ mesons by various substances. Slowing down in the material, $\mu^-$ mesons are finally taken into the atomic orbits, thus forming $\mu$-mesic atoms. The capture usually occurs first on orbits with large quantum numbers ($n = 10$-$15$), and then, in a number of cascade transitions with the radiation of $\mu$-meson X-rays, the $\mu^-$ meson goes « down the stairs » to the $K(1_s)$ shell of the atom, i.e. to the ground state. The radius of each mesoatom orbit is about 200 times less than that of the corresponding electron orbit (the ratio of the masses of the $\mu$ and electron). Thus, for example, the radius of the first mesoatom orbit for mesohydrogen, $H\mu^-$ (in which the only electron of the H atom is substituted by $\mu^-$) is equal to $2.5 \times 10^{-11}$ cm. With so small a radius, close to nuclear dimensions, the atom of mesohydrogen behaves as a single electrically neutral particle. It may be brought close to various nuclei and interacts without any hindrance caused by electrostatic repulsion of the nucleus and proton. As a result, mesohydrogen may serve as a catalyst for cold mesonuclear synthesis of helium from hydrogen [for a review, see ref. 21].

A decrease of distance between $\mu^-$ and proton causes, of course, a corresponding increase in all transition energies of the mesoatom as compared to transitions in ordinary atoms (e.g. the ionisation potential of mesohydrogen is close to 2.5 KeV). Each mesoatom has its characteristic X-ray spectrum. Besides, the lifetime of the $\mu^-$ meson occupying the $1_s$ shell is also a characteristic function of the atomic number $Z$, as the observed lifetime

$$T = \frac{1}{\dfrac{1}{T_0} + \dfrac{1}{T_2}}, \qquad T_0 = 2.2 \times 10^{-6}\ \text{sec.}$$

$T_0$ is the lifetime of the $\mu^\pm$ in vacuo, and $T_2$, depending on $Z$, is the characteristic time of $\mu^-$ meson capture by any of the nuclear protons: $\mu^- + p \rightarrow n + \nu_\mu$.

It is possible to determine the branching ratios of $\mu^-$ capture by different components by observation of the half life of the $\mu^-$ in various complex substances, and especially the $\mu$-mesonic X-ray spectrum. Theoretical speculations were made to the effect that the probability of cap-

ture by the $i$th component of a complex system is given by $W_i \frac{n_i Z_i}{\sum n_i Z_i}$, where $n_i$ is the concentration of the $i$th component and $Z_i$ its atomic number. Numerous experiments showed, however, that this formula (the so-called $Z$-law of Fermi and Teller) is but a rare exception, well satisfied only for metallic alloys. Detailed study by Dubna scientists of the probability of $\mu^-$ capture by more than 20 different elements with $Z = 4$-$82$ and oxygen in oxides of normal valence led to the conclusion that the ratio of probabilities of $\mu$-meson capture $W(Z) : W(O)$ is of periodic character. The experimentally determined ratio $W(Z)/W(O) = f(Z)$ is given in Fig. 7.

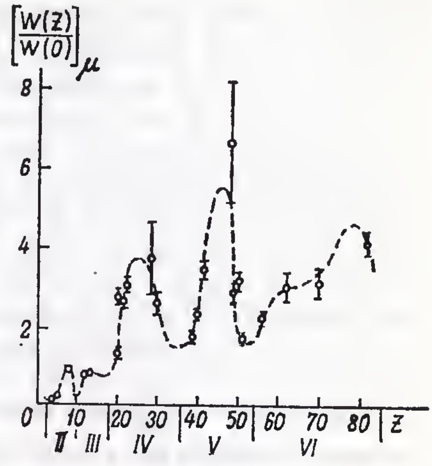


Fig. 7.

Ratios of probabilities of atomic capture of $\mu^-$ mesons in oxides. $W(Z)$ and $W(O)$ are probabilities of capture for a nucleus $Z$ and oxygen respectively.

This periodic character is quite unexpected if one assumes that the mesons go directly into atomic orbits. It has, however, a satisfactory explanation (at least qualitatively) in the model of large mesic molecules as suggested by L. I. Ponomarev [22]. According to this model, the mesons are captured first not on mesoatomic levels, but on joint mesomolecular levels whose quantum numbers are so large that they correspond to normal interatomic distances ($\sim 10^{-8}$ cm) despite the 200 times smaller scale of $\mu$-mesic atoms as compared with ordinary ones. Thus, the $\mu^-$-meson finds itself in a non-symmetric double potential well (Fig. 8) and successively cascades to the region where the mesolevels of the two atoms are well separated. Its final destination depends then on the properties of the electron shells of both atoms. When one of the atoms is fixed (in this case oxygen), and the other is varied, the periodic structure of the external shells in such a model may lead to the periodicity of the probability ratio $(W(Z)/W(O))_\mu$.

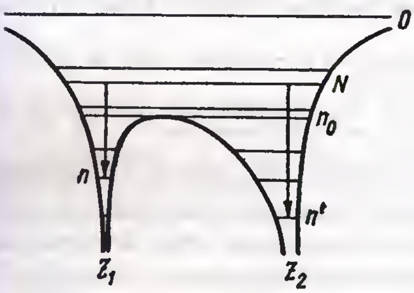


Fig. 8.

Meson levels in asymmetric two-atom molecule $Z_1Z_2$. Levels situated above $n_0$ are general mesomolecular levels, and below $n_0$-mesoatomic levels of $Z_1$ and $Z_2$.

This model of large mesic molecules has also been applied to the problem of the regularities in the capture of slow $\pi^-$ mesons in mixtures and chemical compounds containing hydrogen. In hydrogen, about 60% of events is accompanied by charge exchange: $\pi^- p \rightarrow \pi^0 n$, (while in the other 40% the capture proceeds via the mechanism: $\pi^- + p \rightarrow \gamma + n$). The slow $\pi^0$-meson then immediately decays into two photons moving in opposite directions with energy 70 MeV. In $\pi^-$-capture by complex nuclei, neither of the above processes occur, but the $\pi^-$-capture is accompanied by the emission of many nucleons. Thus, determination of the number of $\pi^0$-mesons, by detecting the two-photon coincidences, serves as a reliable determination of the fraction of $\pi^-$ mesons captured by the hydrogen atoms. In experiments carried out in the Laboratory of Nuclear Problems in Dubna in 1962-1965 [23, 24, 25] it was shown that the ratio of probabilities of capture of slow $\pi^-$ mesons by protons and nuclei with charge $Z$, the ratio $[W(H)/W(Z)]_\pi$ is very different for simple mixtures and chemical compounds of $Z$ and $H$. If in mixtures $Z_m + (H_2)_n$, the probability ratio is $[W(H)/W(Z)]_\pi \approx \frac{2n}{mZ}$, in a binary compound of similar substances this ratio is reduced by a factor of about $Z^2$. For example, in a mixture of gases $N_2 + 2H_2$, the probability of $\pi^-$-capture is 30% and in $N_2H_4$, this probability decreases up to about $\frac{1}{200}$. An even more interesting feature is that the ratio $[W(H)/W(Z)]_\pi$ proved to be dependent on the nature of the chemical bond. The ratio $[W(H)/W(Z)]_\pi$ is 2.5 times greater for ethylene $C_2H_4$ than for acetylene $C_2H_2$, rather than 2 times grater. Thus we see that the difference between the two types of bonds $H_2C = = C\begin{smallmatrix} / H \\ \backslash H \end{smallmatrix}$ and $HC \equiv C—H$ is of importance in $\pi^-$-capture, and is related to the larger energy of the C—H bond in acetylene as compared to ethylene.

So far, experiments on $\mu^-$ and $\pi^-$-capture are limited to studying the influence of already known properties of various compounds on capture characteristics. Nuclear chemistry is now faced with the problem of learning how to use the properties of mesoatom systems to obtain as yet unknown properties of chemical bonds.

***

In this article, we have examined the connection of the Mendeleev periodic system with some of the problems of present-day nuclear chemistry. It appears more and more to be a field of physical chemistry which is concerned with the study of mutual connections and influences of trans-

formations of atomic nuclei and elementary particles, and the properties of their molecular and crystalline environment. There is no doubt that further studies of the Mössbauer effect using a greater number of different isotopes will allow to understand more clearly the laws for changes in electron densities near nuclei, in the gradients of internal molecular electric fields and the values of internal molecular magnetic fields in different compounds of elements in various groups and periods of the Mendeleev table. The obtaining of this type of information is also promised by a systematic chemical uses of the method of perturbed angular correlations. The study of the effect of chemical bonding on the lifetimes of radioactive isotopes undergoing electron capture or internal electron conversion, and on conversion coefficients for various shells, ceases to be exotic pursuits. These processes must also be influenced by regularities of changes in the structure of valence shells of atoms tied chemically to the radioactive ones. Study of the influence of valence shells on the energy required for the removal of internal electrons and on the energy of characteristic X-ray lines have a great future. It is still too early to speak of concrete outlines and the connections between numerous new phenomena of nuclear chemistry and the Mendeleev periodic system. It is first necessary to accumulate much more experimental data. However, the examples from the chemistry of new atoms and new elements where these connections are more or less clear are already sufficient to see the fundamental role played by the work of D. I. Mendeleev in quite new fields of chemistry which appeared and have been developed many decades after the death of the brilliant creator of the periodic system of elements.

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C. MOORE-SITTERLY (*)

# The Periodic Table Interpreted from Atomic Spectra.

Nature has provided a powerful tool for probing into the outer structure of atoms through the medium of optical spectra. The radiation from different atoms and ions produced by various light sources such as an electric arc, and electrodeless lamp, a sliding spark, a plasma, etc. when examined with the spectroscope reveals the properties of the valence electrons. The secret of this method lies in the fact that the spectrum of each atom or ion is unique—it is a pattern of lines whose wavelengths and relative intensities are characteristic of that and only that atom or ion.

Details of the well-established Hund Theory of Line Spectra need not be given here. The interpretation of a spectrum requires the wavelength measurement of the observed lines, the conversion of the wavelengths to wave numbers in vacuo, and a search among the wave numbers for common differences. Each observed line results from a transition of outer electrons between two energy levels. The energy levels are derived from the repeated common differences. A limited number of energy levels can account for a large number of observed lines. By means of certain rules from the quantum theory, the levels are grouped into terms from which, in turn, the corresponding configurations of the outer electrons can be determined. Various criteria are used in establishing the terms, such as relative line intensities, splitting of lines when observed in a magnetic field (Zeeman effect), combining properties, and the like. A limited number of general regularities in atomic spectra suffice to illustrate the order that prevails throughout the Periodic Table. Many arrangements of this Table are used to describe the various atoms and elements. The Periodic Chart as given in Table I [1] shows the atoms grouped according to the number of outer electrons. It is, therefore, particularly suitable as a basis for discussing atomic spectra.

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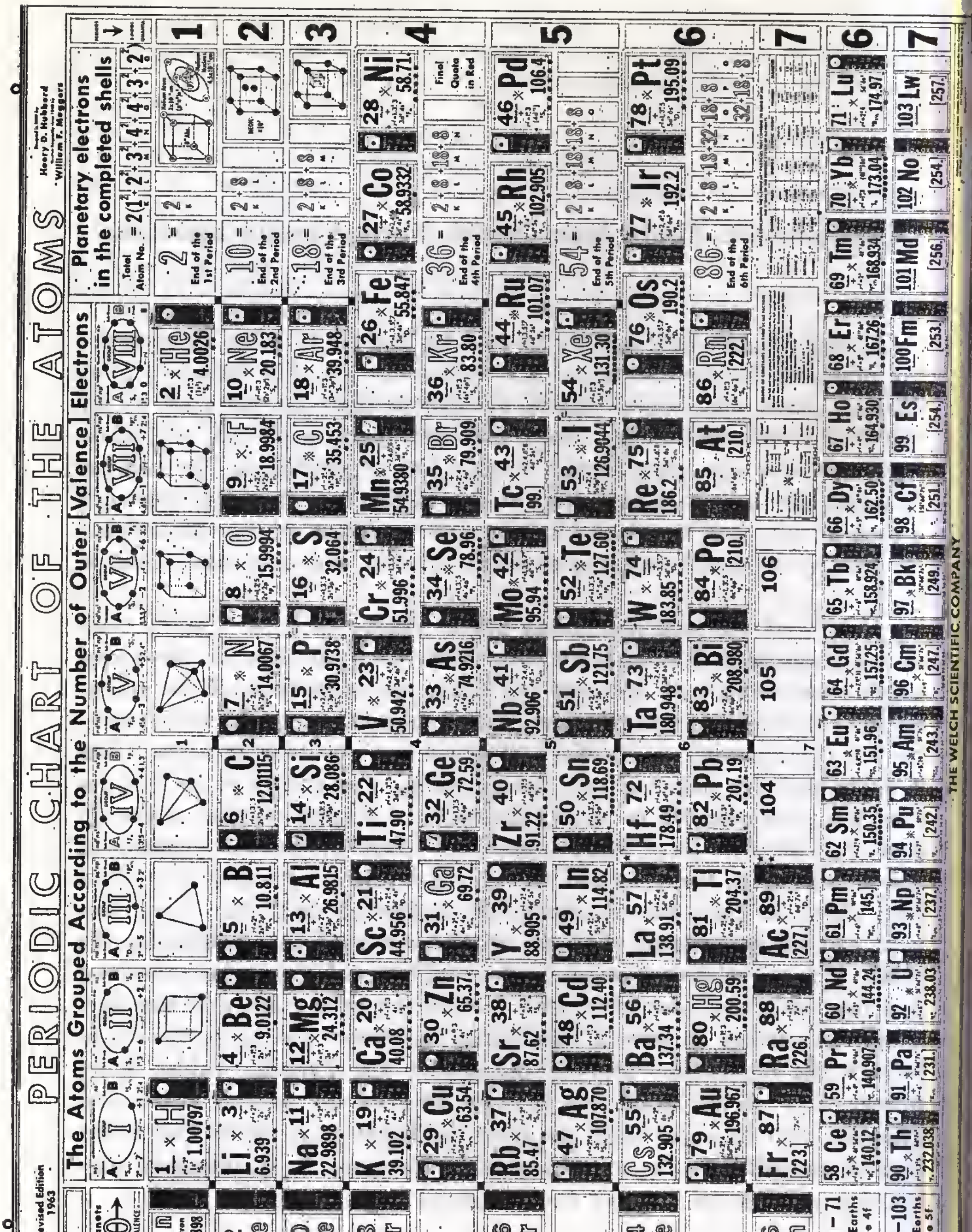
(*) U.S. Department of Commerce, National Bureau of Standards, Washington, D. C. (U.S.A.).

TABLE I (*).


PERIODIC CHART OF THE ATOMS
The Atoms Grouped According to the Number of Outer Valence Electrons
Planetary electrons in the completed shells
Revised Edition 1963
THE WELCH SCIENTIFIC COMPANY

## The Vertical Groups in the Periodic Chart.

« Among the first regularities to be discovered in atomic spectra was the occurrence of series of lines in which the intervals between successive lines, and their intensities decrease in a more or less regular manner toward shorter wavelengths, so as to make the series converge toward a definite limit » [2].

For the simpler spectra like those of H I and He I, where only one or two outer electrons are effective, the line series converging to different limits can be detected by visual inspection of the spectrograms. The series in H I are shown graphically in figure 1, which is a Grotrian Diagram of the spectrum [3]. The horizontal lines indicate the energy levels arising from the configurations $1s$; $2s$, $2p$ etc. The ordinates are given in both $cm^{-1}$ and eV. Vertical lines represent the wave numbers of the lines whose wavelengths are indicated in the figure. The sixth and highest observed series is produced by lines in the far infrared near $12.37\ \mu$.

The spectra of elements in the first column consist of long doublet series. They resemble each other because of the similarity in electronic structure. The ground states of the first spectra are, respectively:

| Li I | Na I | K I | Rb I | Cs I |
|---|---|---|---|---|
| $2s\,^2S_{0\,1/2}$ | $3s\,^2S_{0\,1/2}$ | $4s\,^2S_{0\,1/2}$ | $5s\,^2S_{0\,1/2}$ | $6s\,^2S_{0\,1/2}$. |

« The running series number starting with 2 for Li I and 6 for Cs I corresponds to the principal quantum number $n$, which measures the angular momentum of the electron's motion in a circular orbit, the radius of which is proportional to $n^2$ ». The azimuthal quantum number $l$ in the Bohr-Sommerfeld theory accounts for the shape of the orbit. The electron orbits with $l = 0, 1, 2, 3$ etc. are designated by the letters $s$, $p$, $d$, $f$ etc. which describe the running electrons. « In $LS$-coupling the vectors are coupled by electrostatic interaction to form the total (orbital) angular momentum $L$... and the total spin $S$... $L$ and $S$ then combine by magnetic interaction to a total angular momentum $J$... », the inner quantum number. When $L$ is sufficiently large the total of fine structure components is $2S + 1$; this number is called the multiplicity. Term designations, are, thus, described as $^{2S+1}L_J$, as denoted above for the ground terms of Li I etc. Examples of $LS$ term designations are given in Table II, which is from B. Edlén [2].

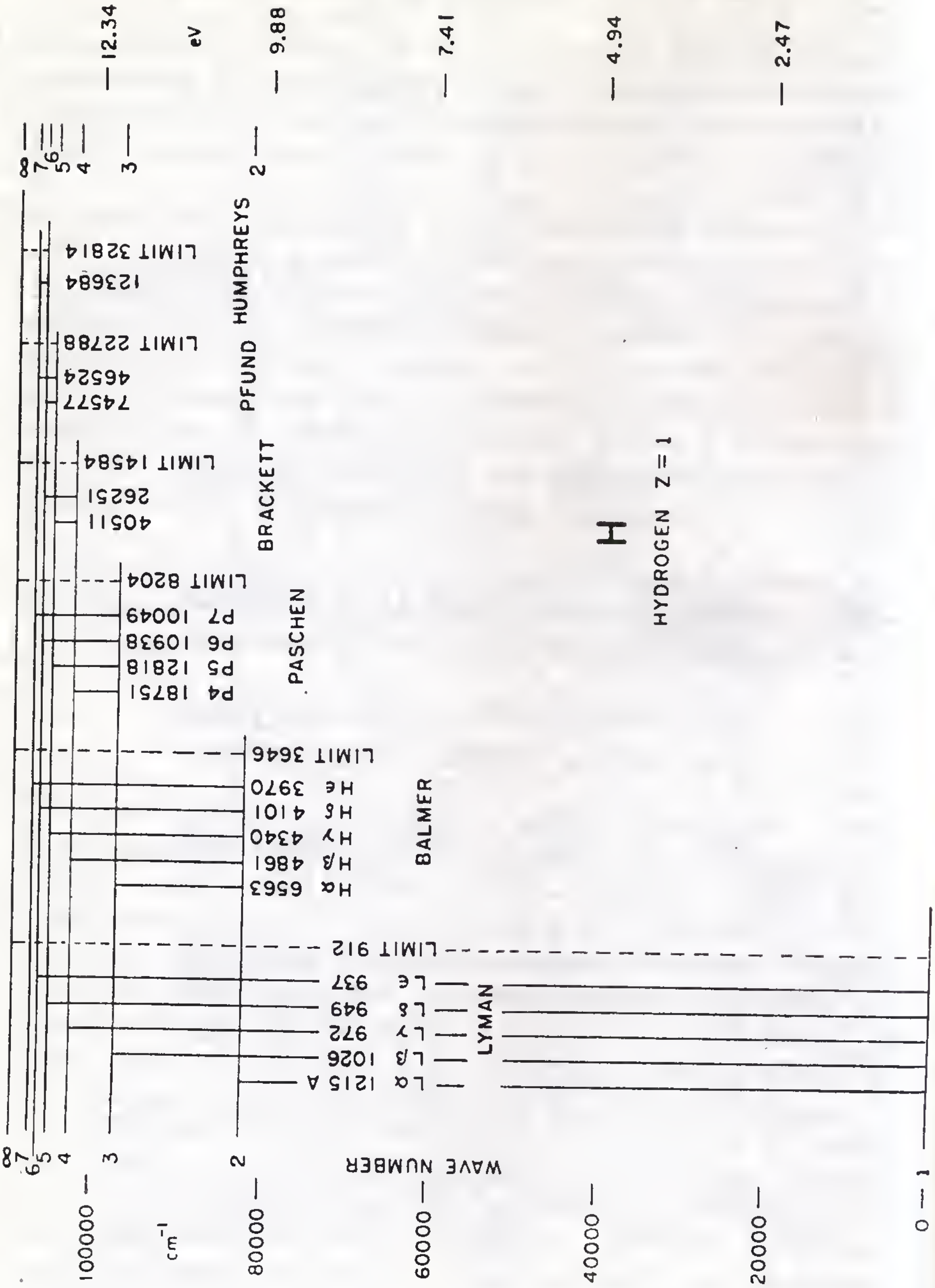

H
HYDROGEN Z = 1
eV
12.34
9.88
7.41
4.94
2.47
0.00
cm⁻¹
WAVE NUMBER
100000
80000
60000
40000
20000
0
LYMAN
Lα 1215 A
Lβ 1026
Lγ 972
Lδ 949
Lε 937
LIMIT 912
BALMER
Hα 6563
Hβ 4861
Hγ 4340
Hδ 4101
Hε 3970
LIMIT 3646
PASCHEN
P4 18751
P5 12818
P6 10938
P7 10049
LIMIT 8204
BRACKETT
40511
26251
LIMIT 14584
PFUND
74577
46524
LIMIT 22788
HUMPHREYS
123684
LIMIT 32814
∞
7
6
5
4
3
2
1

Fig. 1.

TABLE II. — *LS designations of terms and levels.*

| | L = 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| S = 0 | $^1S_0$ | $^1P_1$ | $^1D_2$ | $^1F_3$ | $^1G_4$ |
| ½ | $^2S_{1/2}$ | $^2P_{1/2,\,3/2}$ | $^2D_{3/2,\,5/2}$ | $^2F_{5/2,\,7/2}$ | $^2G_{7/2,\,9/2}$ |
| 1 | $^3S_1$ | $^3P_{0,\,1,\,2}$ | $^3D_{1,\,2,\,3}$ | $^3F_{2,\,3,\,4}$ | $^3G_{3,\,4,\,5}$ |
| 1½ | $^4S_{3/2}$ | $^4P_{1/2,\,3/2,\,5/2}$ | $^4D_{1/2,\,\ldots,\,7/2}$ | $^4F_{3/2,\,\ldots,\,9/2}$ | $^4G_{5/2,\,\ldots,\,11/2}$ |
| 2 | $^5S_2$ | $^5P_{1,\,2,\,3}$ | $^5D_{0,\,1,\,2,\,3,\,4}$ | $^5F_{1,\,2,\,3,\,4,\,5}$ | $^5G_{2,\,3,\,4,\,5,\,6}$ |

The first spectra of the next vertical group of elements are more complex. The ground states are produced by two equivalent *s*- electrons. Two multiplicities occur, giving rise to singlet and triplet terms:

| | Be I | Mg I | Ca I | Sr I | Ba I | Ra I |
|---|---|---|---|---|---|---|
| Ground Term: | $2s^2\ ^1S_0$ | $3s^2\ ^1S_0$ | $4s^2\ ^1S_0$ | $5s^2\ ^1S_0$ | $6s^2\ ^1S_0$ | $7s^2\ ^1S_0$ |
| Higher Terms: | $2p\ ^3P^o$ | $3p\ ^3P^o$ | etc. | | | |
| | $2p\ ^1P^o$ | $3p\ ^1P^o$ | etc. | | | |

Mg I is of special interest. Although series in this spectrum were known for years, only the leading members of the $^1F^o$ and $^3F^o$ series were observed in the laboratory. F. Paschen recorded six members of the series $3d\ ^1D - nf\ ^1F^o$ and two of the corresponding triplet series. These and numerous other lines of Mg I are clearly present in the solar spectrum, where they appear as wide and diffuse lines. With the aid of the known Rydberg denominators of the $nf\ ^{1,3}F^o$ series, i. e., the series formula derived from the wave numbers of the known laboratory lines, it was possible to extend the series by using infrared solar wavelengths. Thus, in 1934, long before the lines were observed in the laboratory, these series were extended to $n = 12$ [4], and in 1945 to $n = 14$ [5].

In this group of elements the first spectra of Ca, Sr, and Ba, provided a far-reaching insight into electronic structure in the Periodic Table. After the regular series had been found, i.e., those converging to the ground term of the ion ($^2S$), many lines still remained unclassified. H. N. Russell and F. A. Saunders [6] first discovered that these lines were due to transitions involving a double-electron jump. The new series converged to the next lowest term in the ion as limit, a metastable $^2D$ term, thus showing that « a neutral atom can contain more than enough energy to ionize it ». « Both valency electrons may jump at once from outer to inner orbits while the net energy lost is radiated as a single quantum - the atom acting

as a whole ». Configurations involving two excited electrons are now commonly known in complex spectra throughout the Periodic Table.

As more outer or valence electrons are added, the spectra become increasingly complex, and different types of regularities appear. For example, the observed spectra of the inert gases have ground configurations in which the electrons are in filled shells:

| | He I | Ne I | Ar I | |
|---|---|---|---|---|
| Ground state | $1s^2\ ^1S_0$ | $2p^6\ ^1S_0$ | $3p^6\ ^1S_0$ | etc. |

From Ne I through Rn I the higher energy levels reveal the effects of « pair » coupling ($jl$). The interval of the limit term of the ion is clearly reflected in the level structure, and the series consist of pairs of levels having the components of the limit term as limit. The following example is from Ne I:

| Configuration | LS | $J$ | Level | $J$ | | Limit (Ne II) | Interval |
|---|---|---|---|---|---|---|---|
| $2p^5(^2P^o)3s$ | $^3P^o$ | 2 | 134043 | 2 | 777 | $^2P^o_{3/2}$ | 782 |
| | | 1 | 134461 | 1 | | $^2P^o_{1/2}$ | |
| | | 0 | 134820 | 0 | | | |
| | $^1P^o$ | 1 | 135890 | 1 | | | |

Two miscellaneous examples of complex spectra that are of special astrophysical interest deserve mention. One example is concerned with Zeeman patterns, i.e., regular patterns of line-splitting due to the effect of a magnetic field. The number of observed components and their pattern of arrangement depend upon the quantum numbers in the designation of the classified line. The familiar Landé $g$-values are derived from the Zeeman patterns.

Selected lines in Cr I and the rare-earth spectrum Eu II, (elements that are widely separated in the Periodic Table) have striking Zeeman patterns. In each spectrum there are three very intense resonance lines produced by transitions from a ground S-term to a higher P-term:

Cr I $3d^5(S^6)4s\ ^7S$ — $3d^5(^6S)4p\ ^7P^o$ $\lambda\lambda$ 4254, 4274, 4289

Eu II $4f^7(^8S^o)6s\ ^9S^o$ — $4f^7(^8S^o)6p\ ^9P$ $\lambda\lambda$ 3819, 41329, 4205.

These lines are in a region accessible for observation in stellar spectra. The term designations are such that when the lines are observed in a magnetic field, the Zeeman patterns consist of numerous widely separated components.

An interesting group of stars known as magnetic stars, mostly of spectral class *A*p, discovered by H. W. Babcock, exhibit periodic changes in magnetic field accompanied by variations in intensity of their spectral

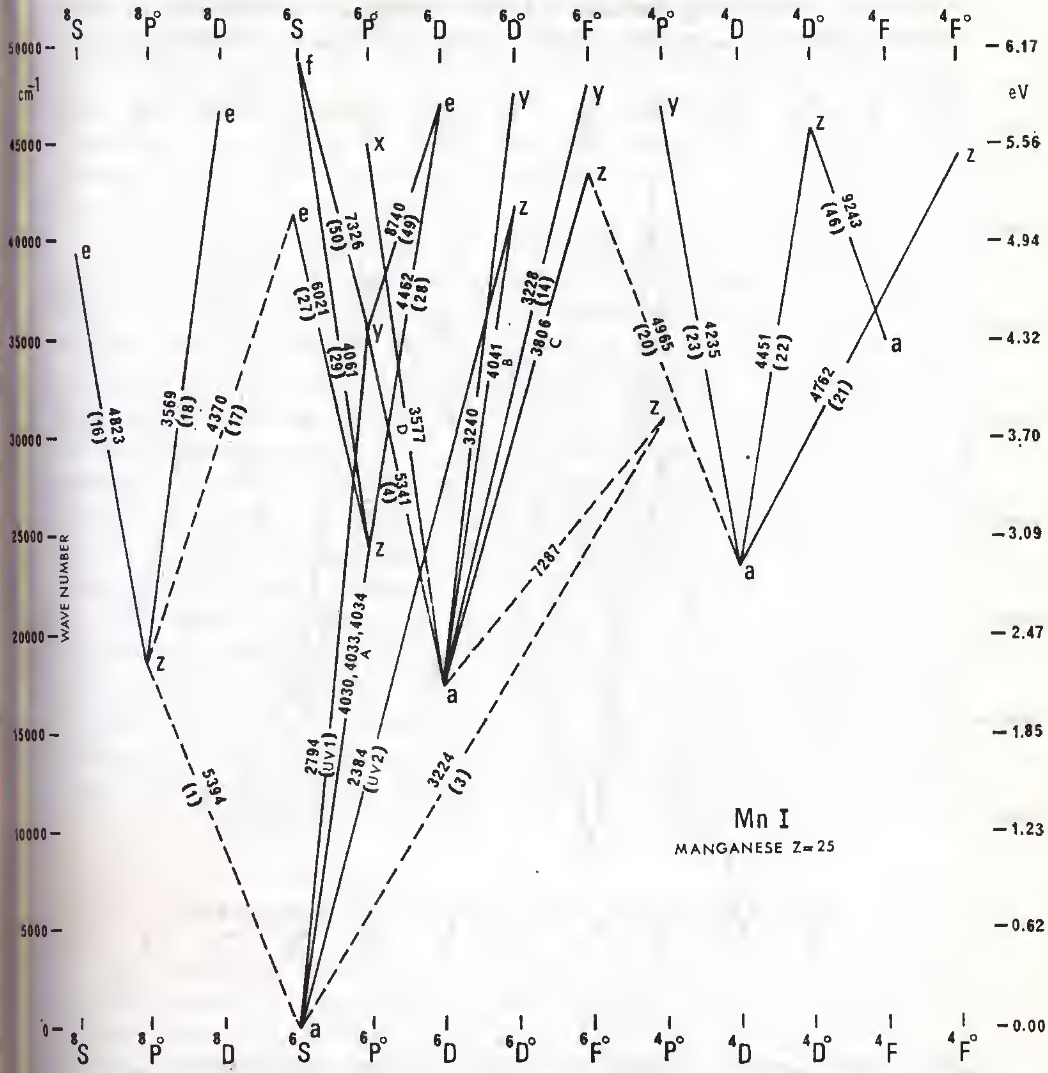



Fig. 2.

lines. In 1951 [7] he reported that the star HD 125248, whose periodic variation of line intensity is 9.295 days, reached the positive extreme (+ 7000 gauss) near zero phase of the period, when Eu II lines attain maximum intensity, and the negative extreme (— 6200 gauss) at mid-period when lines of Eu II are weak and those of Cr I and Cr II are at

maximum intensity. In another star, $\alpha^2$ Can Ven (Period 5.469 days) the reverse is true as regards intensity behavior of these lines.

Babcock has stated that the Eu II lines are particularly susceptible to Zeeman broadening because of the numerous components in their Zeeman patterns, more than 20 for $\lambda$ 4205 [7]. The Cr I line $\lambda$ 4254 has,

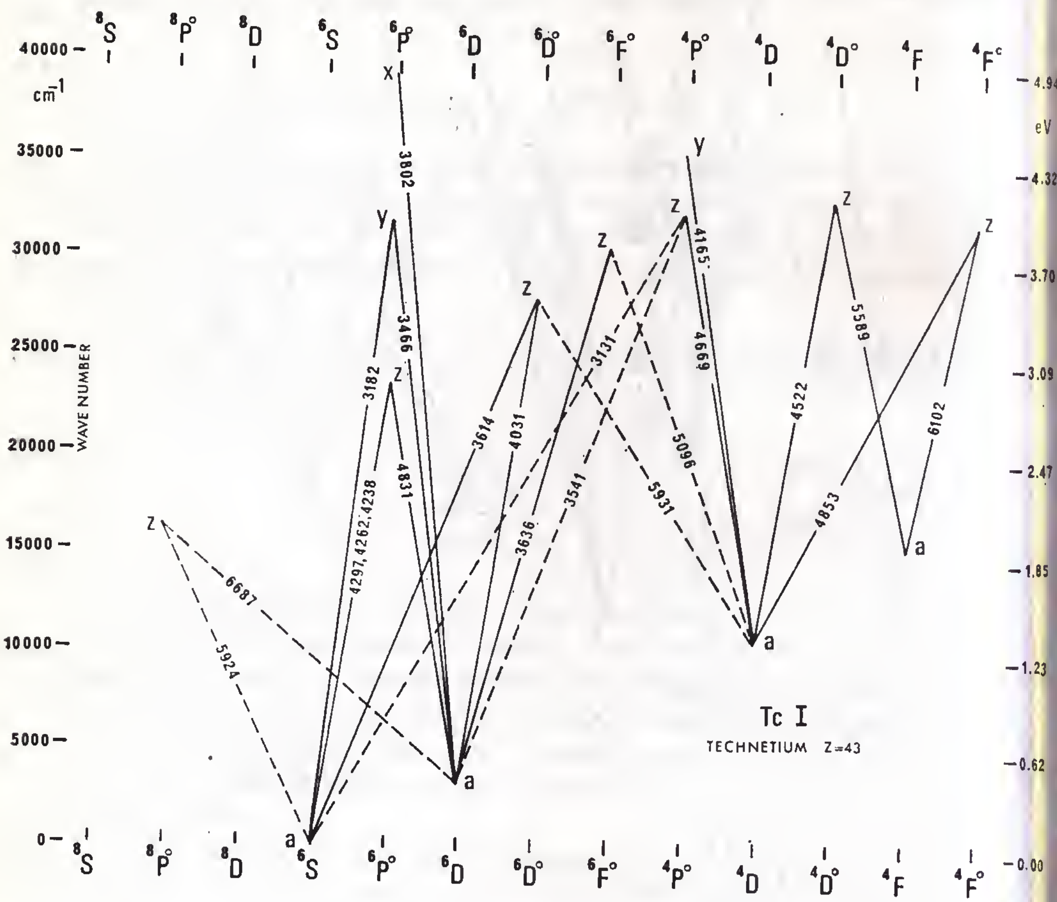



Fig. 3.

also, a wide Zeeman pattern. He points out that the intensity may be increased several fold in a magnetic field of a few kilogauss because the Zeeman pattern may be considerably wider than the Doppler broadening of the stellar lines [8]. This regularity in the Zeeman effect may be one factor that contributes to the peculiar periodic intensity variation of these lines.

Another curious example is furnished by the element technetium ($Z = 43$), an artificially produced element for which no long-lived isotope

has yet been found. Nevertheless, Tc I lines have been identified unquestionably in the spectrum of R And, an *S*-giant star [9]. The appearance of this element in stars presents an interesting problem in stellar structure and is not well understood in detail.

Remarkable similarities exist in complex spectra, as is well illustrated by the spectra Mn I and Tc I in vertical Group VII of Table I. In 1922 M. A. Catalán discovered « multiplets » in the spectra Mn I and Mn II [10]. A multiplet is a group of related lines; the relations are determined on the basis of the quantum theory. The groups of Cr I and Eu II lines shown above are examples of multiplets.

The resemblance between the spectra Mn I [3] and Tc I [11] can be seen by comparing the partial Grotrian diagrams of these spectra, shown in figures 2 and 3. The positions of the various terms are plotted in $cm^{-1}$, the ordinate in the figures. The abscissae show the different types of terms, each of which is made up of one or more energy levels. The transitions producing the groups of related lines in the optical spectra are indicated by the diagonal lines, each of which represents a multiplet. The vertical distances between the points connecting the lines indicate the wave numbers of the leading member of each group. The numbers entered along the lines in the diagrams give the wavelengths in Å corresponding to the respective wave numbers.

The general features in these two diagrams resemble each other. One striking difference, however, is that the lowest $^6D$ term is much lower in Tc I [11] than in Mn I. The transition $a\,^6D - z\,^6P^o$ would produce infrared lines in Mn I, whereas in Tc I the lines are in the visible spectral range, $\lambda 4831$ on the diagram. The same is true of some other combinations, but over and above this, the similarities exhibited in these complex spectra are remarkable.

## Horizontal Arrangement of the Periodic Chart.

The electronic structure of the periodic system is shown simply in Table I where the atoms are grouped according to the number of outer (valence) electrons. A glance at the rows in this Chart reveals the building on of electrons as the atomic number $Z$ increases. This in turn results in the gradual increase in complexity of the atomic spectra. This subject is clearly presented in detail by G. Herzberg [12] who summarizes it with the statement that « the whole periodic system of the elements can be unambiguously derived by using the building-up principle in conjunction with the Pauli principle ».

One of the simplest illustrations of regularities in structure may be found from a plot of the principal ionization potentials in the first

spectra of the elements H through Ca ($Z = 1$ to 20) (figure 4). The « principal » ionization potentials represent the difference in energy between the normal states of the atoms in successive degrees of ionization. The well-known changes in energy as the *s*- and *p*-shells become filled are striking. The decrease in energy when the *p*-shells are half-filled is, also, conspicuous. From B I to N I the multiplicity increases to its maximum value as successive 2*p*-electrons are added. From O I to Ne I, because

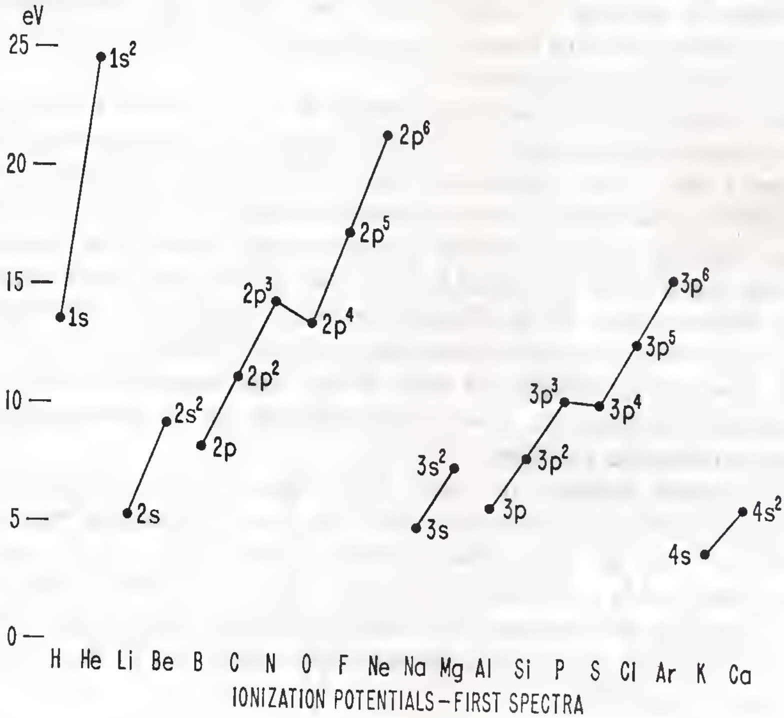



Fig. 4.

of Pauli's exclusion principle, it decreases. The magnetic force changes sign where the observed discontinuity occurs — an effect of electron spin.

This effect [13] has been described in more detail by Russell in a paper on *Series and Ionization Potentials of the Elements of the Iron Group*, where the shell of 3*d*-electrons is discussed. The change in term structure as this shell is filled is illustrated in Table III, where selected regularities in two spectra are shown: in Cr I four 3*d*-electrons are involved and in Mn I six 3*d*-electrons are effective. In Cr I the level intervals increase regularly with increasing value of the inner quantum number *J*. In Mn I the term is inverted, i.e., the lowest level in the group has the largest

TABLE III.

| Config. | Desig. | J | Level | Interval |
|---|---|---|---|---|
| | | Cr I | | |
| $3d^5(^6S)4s$ | $a\ ^7S$ | 3 | 0.00 | |
| $3d^5(^6S)4s$ | $a\ ^5S$ | 2 | 7 593.16 | |
| $3d^4\ 4s^2$ | $a\ ^5D$ | 0 | 7 750.78 | |
| | | 1 | 7 810.82 | 60.04 |
| | | 2 | 7 927.47 | 116.65 |
| | | 3 | 8 095.21 | 167.74 |
| | | 4 | 8 307.57 | 212.36 |
| | | Mn I | | |
| $3d^5\ 4s^2$ | $a\ ^6S$ | $2\frac{1}{2}$ | 0.00 | |
| $3d^6(^5D)4s$ | $a\ ^6D$ | $4\frac{1}{2}$ | 17 052.29 | |
| | | $3\frac{1}{2}$ | 17 282.00 | − 229.71 |
| | | $2\frac{1}{2}$ | 17 451.52 | − 169.52 |
| | | $1\frac{1}{2}$ | 17 568.48 | − 116.96 |
| | | $0\frac{1}{2}$ | 17 637.15 | − 68.67 |

*J*-value. The inversion is typical when a shell is more than half-filled, in this case, the shell of the ten *d*-electrons.

B. Edlén has published [2] an arrangement of the Periodic Table that reveals the electron structure quite simply (Table IV).

*Isoelectronic Sequences*: Brief mention has already been made of the run of ionization potentials as the shell of $2p$-electrons is being filled (figure 4). An extensive compilation of revised ionization potentials, together with the first ionization limits is in course of preparation. A sample is shown in Table V. For the benefit of those who need information on higher limits the energy levels of the lowest configuration from the ground state zero, are included. The higher limits are particularly useful for the interpretation of well-developed series observed in absorption in the far ultraviolet.

This limited sample introduces another type of regularity exhibited by optical spectra, namely, that along the isoelectronic sequences, where the electron structure is identical, but the ionization stage increases. In Table V the similarity in the terms listed for C I, N II, O III, F IV and for N I, O II, F III is striking.

Graphically, this is well illustrated by the Grotrian diagrams. The simplest case is that of the H I sequence where there is only one outer

electron. The familiar H I diagram has been shown above (figure 1). In He I the ground configuration is $1s^2$; in He II, Li III, etc. it is identical with that of H I, namely $1s$. The diagram for He II [3] resembles closely that of H I except for the change in scale of the energy levels (figure 5).

TABLE IV. — *Periodic system of the elements.*

| (1s) | (2s) (2p) | (3s) (3p) | (4s, 3d) (4p) | (5s, 4d) (5p) | (6s, 4f, 5d) (6p) | (7s, 5f, 6d) (7p) | |
|---|---|---|---|---|---|---|---|
| 1 H | 3 Li | 11 Na | 19 K | 37 Rb | 55 Cs | 87 Fr | $s$ |
| 2 He | 4 Be | 12 Mg | 20 Ca | 38 Sr | 56 Ba | 88 Ra | $s^2$ |
| | | | 21 Sc | 39 Y | 57 La | 89 Ac | $s^2 d$ |
| | | | | | — — — | — — — | $s^2 d f^k$ |
| | | | | | 71 Lu | ..... | $s^2 d (f^{14})$ |
| | | | 22 Ti | 40 Zr | 72 Hf | ..... | $s^2 d^2$ |
| | | | 23 V | 41 Nb | 73 Ta | ..... | $s^2 d^3$ |
| | | | 24 Cr | 42 Mo | 74 W | ..... | $s^2 d^4$ |
| | | | 25 Mn | 43 Tc | 75 Re | ..... | $s^2 d^5$ |
| | | | 26 Fe | 44 Ru | 76 Os | ..... | $s^2 d^6$ |
| | | | 27 Co | 45 Rh | 77 Ir | ..... | $s^2 d^7$ |
| | | | 28 Ni | 46 Pd | 78 Pt | ..... | $s\ d^9$ |
| | | | 29 Cu | 47 Ag | 79 Au | ..... | $s\ (d^{10})$ |
| | | | 30 Zn | 48 Cd | 80 Hg | ..... | $s^2$ |
| | 5 B | 13 Al | 31 Ga | 49 In | 81 Tl | ..... | $p$ |
| | 6 C | 14 Si | 32 Ge | 50 Sn | 82 Pb | ..... | $p^2$ |
| | 7 N | 15 P | 33 As | 51 Sb | 83 Bi | ..... | $p^3$ |
| | 8 O | 16 S | 34 Se | 52 Te | 84 Po | ..... | $p^4$ |
| | 9 F | 17 Cl | 35 Br | 53 I | 85 At | ..... | $p^5$ |
| | 10 Ne | 18 Ar | 36 Kr | 54 Xe | 86 Rn | ..... | $p^6$ |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 Ce | 59 Pr | 60 Nd | 61 Pm | 62 Sm | 63 Eu | 64 Gd | 65 Tb | 66 Dy | 67 Ho | 68 Er | 69 Tm | 70 Yb | $6s^2\ 5d\ 4f^k$ |
| 90 Th | 91 Pa | 92 U | 93 Np | 94 Pu | 95 Am | 96 Cm | 97 Bk | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | $7s^2\ 6d\ 5f^k$ |
| $k = 1$ | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | |

As the stage of ionization increases, more energy is required to produce the successive spectra, and the lines appear at shorter and shorter wavelengths as the sequence progresses. In H I Lyman $\alpha$ is at 1215 Å; in He II the corresponding line is at 303 Å.

Although the spectra of the Li I sequence are more complex, the same trend is shown in the partial Grotrian diagrams. Figure 6 is a graphic

TABLE V.

| $Z$ | Element | I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|---|---|
| 6 | C | $2p^2\,{}^3P_0$ | 90 820.42 ± 0.1 | $2p\ {}^2P^0_0{}^1/_2$ | 196 660 | $2s^2\ {}^1S_0$ | 386 241.0 ± 2 | $2s\ {}^2S_0{}^1/_2$ | 520 178.4 ± 1.5 |
| | | ${}^3P_1$ | 16.40 | ${}^2P^0_1{}^1/_2$ | 63.42 | | | | |
| | | ${}^3P_2$ | 43.40 | | | | | | |
| | | ${}^1D_2$ | 10 192.63 | | | | | | |
| | | ${}^1S_0$ | 21 648.01 | | | | | | |
| 7 | N | $2p^3\,{}^4S^0_1{}^1/_2$ | 117 225.4 | $2p^2\,{}^3P_0$ | 238 750.5 ± 1.3 | $2p\ {}^2P^0_0{}^1/_2$ | 382 704 | $2s^2\,{}^1S_0$ | 624 866 ± 3 |
| | | ${}^2D^0_2{}^1/_2$ | 19 224.464 | ${}^3P_1$ | 48.7 | ${}^2P^0_1{}^1/_2$ | 174.36 | | |
| | | ${}^2D^0_1{}^1/_2$ | 19 233.177 | ${}^3P_2$ | 130.8 | | | | |
| | | ${}^2P^0_0{}^1/_2$ | 28 838.920 | ${}^1D_2$ | 15 316.2 | | | | |
| | | ${}^2P^0_1{}^1/_2$ | 28 839.306 | ${}^1S_0$ | 32 688.8 | | | | |
| 8 | O | $2p^4\,{}^3P_2$ | 109 837.02 ± 0.06 | $2p^3\,{}^4S^0_1{}^1/_2$ | 283 240 | $2p^2\,{}^3P_0$ | 443 086 | $2p\ {}^2P^0_0{}^1/_2$ | 624 383.8 ± 2.0 |
| | | ${}^3P_1$ | 158.265 | ${}^2D^0_3{}^1/_2$ | 26 810.7 | ${}^3P_1$ | 113.9 | ${}^2P^0_1{}^1/_3$ | 385.9 |
| | | ${}^3P_0$ | 226.977 | ${}^2D^0_1{}^1/_2$ | 26 830.5 | ${}^3P_2$ | 306.9 | | |
| | | ${}^1D_2$ | 15 867.862 | ${}^2P^0_1{}^1/_2$ | 40 466.9 | ${}^1D_2$ | 20 274 | | |
| | | ${}^1S_0$ | 33 792.583 | ${}^2P^0_0{}^1/_2$ | 40 468.4 | ${}^1S_0$ | 43 186 | | |
| 9 | F | $2p^5\,{}^2P^0_1{}^1/_2$ | 140 524.5 ± 0.4 | $2p^4\,{}^3P_2$ | 282 058.6 ± 1.5 | $2p^3\,{}^4S^0_1{}^1/_2$ | 505 777 ± 5 | $2p^2\,{}^3P_0$ | 702 830 |
| | | ${}^2P^0_0{}^1/_2$ | 404.1 | ${}^3P_1$ | 341.0 | ${}^2D^0_2{}^1/_2$ | 34 084 | ${}^3P_1$ | 225.2 |
| | | | | ${}^3P_0$ | 489.9 | ${}^2D^0_1{}^1/_2$ | 34 120 | ${}^3P_2$ | 612.2 |
| | | | | ${}^1D_2$ | 20 873.4 | ${}^2P^0_1{}^1/_2$ | 51 558 | ${}^1D_2$ | 25 234.4 |
| | | | | ${}^1S_0$ | 44 918.1 | ${}^2P^0_0{}^1/_2$ | | ${}^1S_0$ | 53 537 |

Ionization Limits-Lowest Terms.

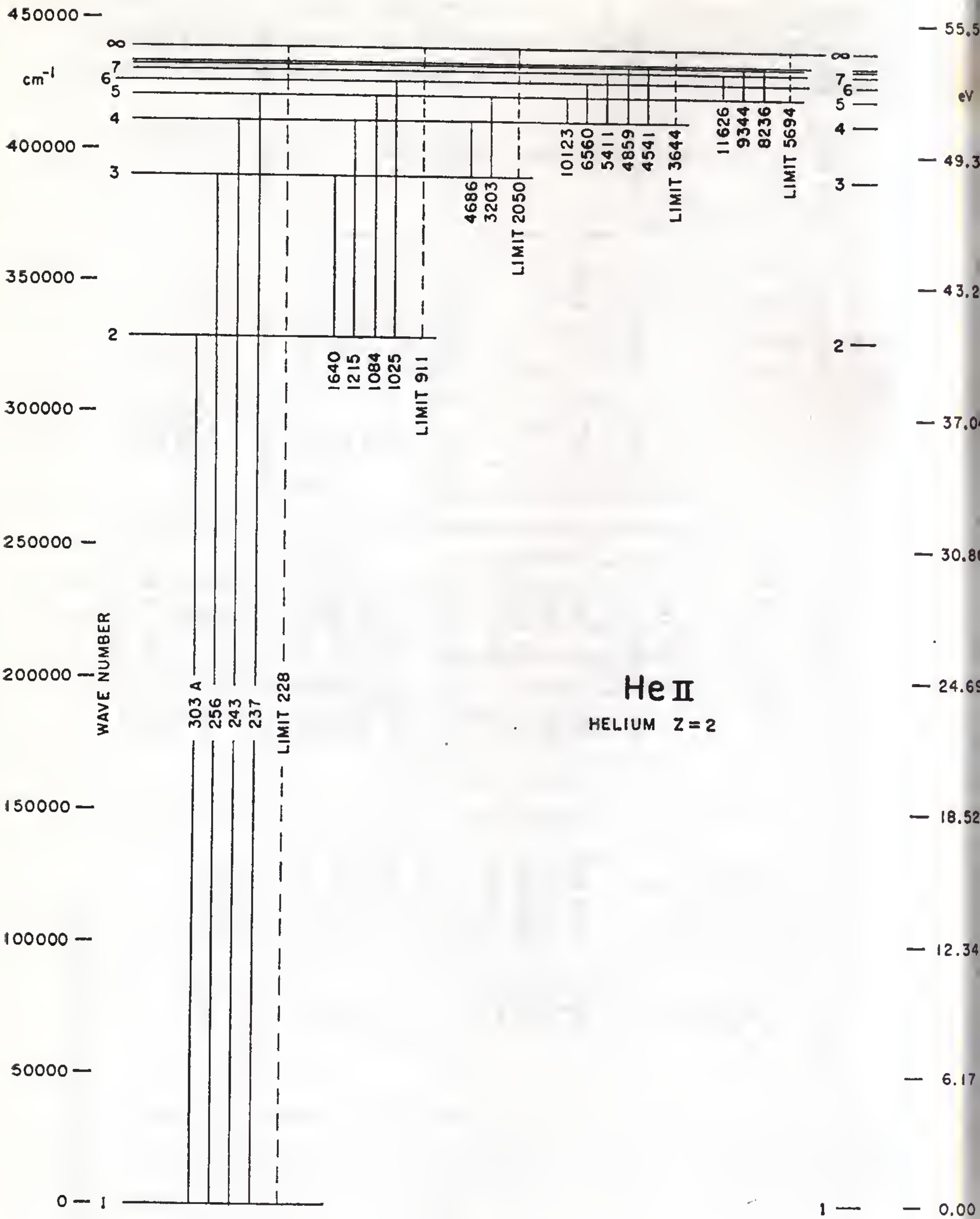

He II
HELIUM Z = 2
WAVE NUMBER
cm⁻¹
eV
303 A
256
243
237
LIMIT 228
1640
1215
1084
1025
LIMIT 911
4686
3203
LIMIT 2050
10123
6560
5411
4859
4541
LIMIT 3644
11626
9344
8236
LIMIT 5694

Fig. 5.

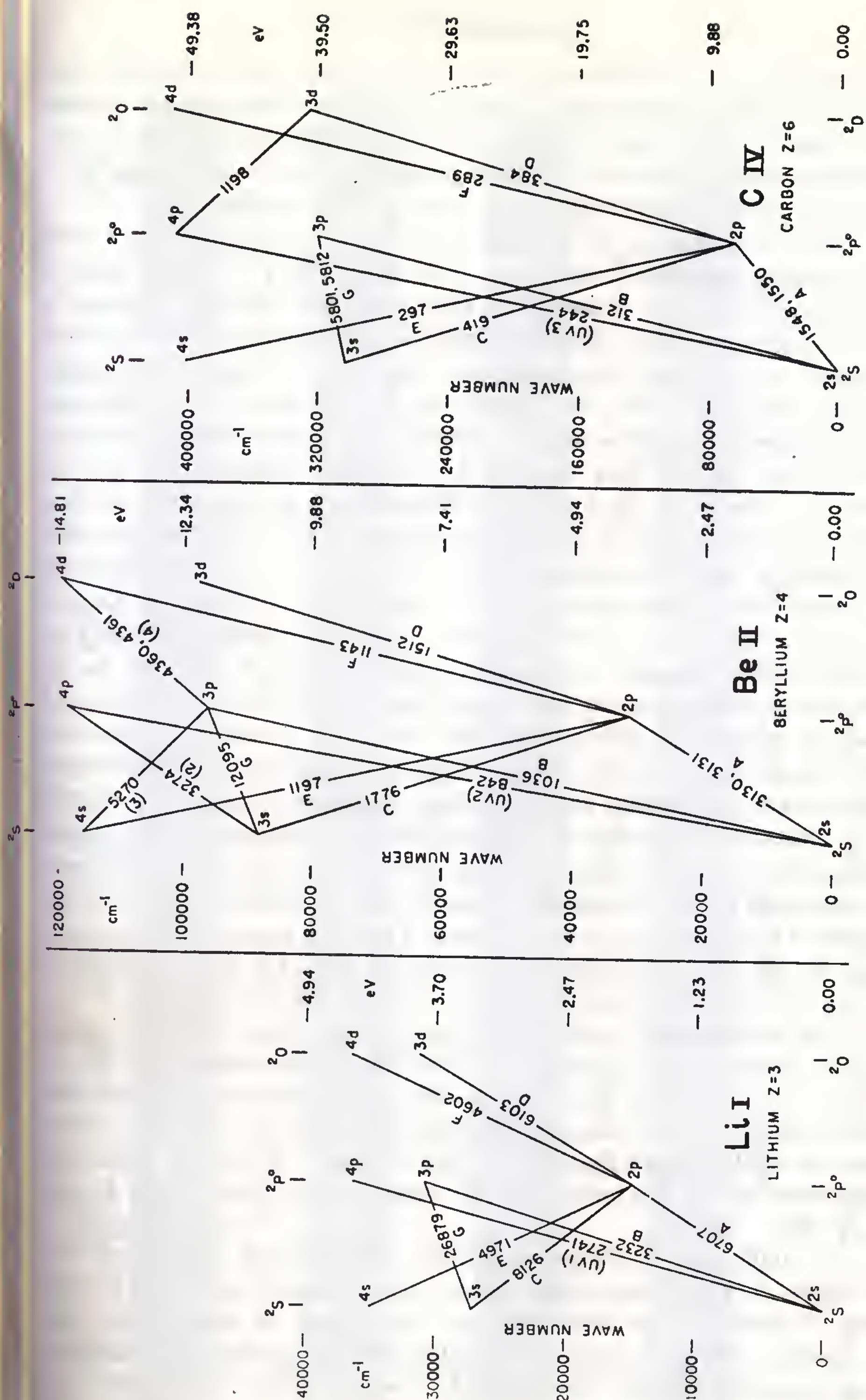

Li I
LITHIUM Z=3
Be II
BERYLLIUM Z=4
C IV
CARBON Z=6
WAVE NUMBER
cm-1
eV

Fig. 6.

presentation of the leading multiplets in Li I, Be II and C IV, all of which have the ground configuration $1s^2\ 2s$. On all of these diagrams the position and type of term are given, and the diagonal lines denote observed combinations giving multiplets. The wavelength of the leading member of the multiplet is indicated for each line on the diagram.

When observations of the solar spectrum were obtained from rockets and orbiting satellites in the range from 3000 Å to 1 Å, a new realm of astrophysics suddenly presented a fascinating and difficult challenge to atomic spectroscopists. Highly-ionized laboratory spectra of abundant elements are required to interpret the solar lines in the « *XUV* » region.

For simpler spectra, the similarities in the spectra of a given isoelectronic sequence can be seen by comparing the spectra directly. Figure 7, taken from Edlén's 1964 monograph [2], shows spectra of Cr, Mn, Fe and Co in the region 90 Å to 40 Å. Related lines in the spectra of three sequences, Na I, Mg I and Al I are clearly marked. In the Na I sequence, for example, the relative intensities in the groups of lines are essentially the same in the successive spectra Cr XIV, Mn XV, Fe XVI and Co XVII.

Such regularities have provided a powerful method not only for spectroscopists engaged in analyzing laboratory spectra, but also for the astrophysicist working on the interpretation of celestial spectra. For years, a number of strong lines observed in the spectrum of the outer solar corona defied identification, although they were in the visible region. Edlén made the brilliant discovery that they were produced by « forbidden » transitions in spectra of the more abundant elements [14]. By careful extrapolation of the interval of the ground term in familiar sequences' he identified them conclusively as due to spectra of highly-ionized atoms. Table VI illustrates the method he used. The wave numbers of the coronal lines fit the extrapolated intervals of the $^2P$ term for Fe XIV and Ni XVI in the Al I sequence, and Fe X and Ni XII in the Cl I sequence.

The increase of the interval along the sequences is plotted against atomic number in the figure below Table VI for the configuration $3s^2\ 3p^n$ ($n = 1, 2, 4, 5$). Table VII gives similar results for the S I sequence, where the intervals in the ground configuration account for more coronal lines of highly ionized Fe and Ni. Below Table VII there is a graphical representation of the origin of the conspicuous coronal lines $\lambda\lambda$ 5303, 6374, 6702, etc.

In 1968, at the Fifteenth Annual Astrophysical Symposium held in Liège, J. T. Jefferies presented a critical compilation of 48 emission lines observed in the solar corona; it contained 20 unidentified lines. B. Edlén published in 1969 [14] a paper confirming earlier identifications and accounting for practically all of these remaining coronal lines.

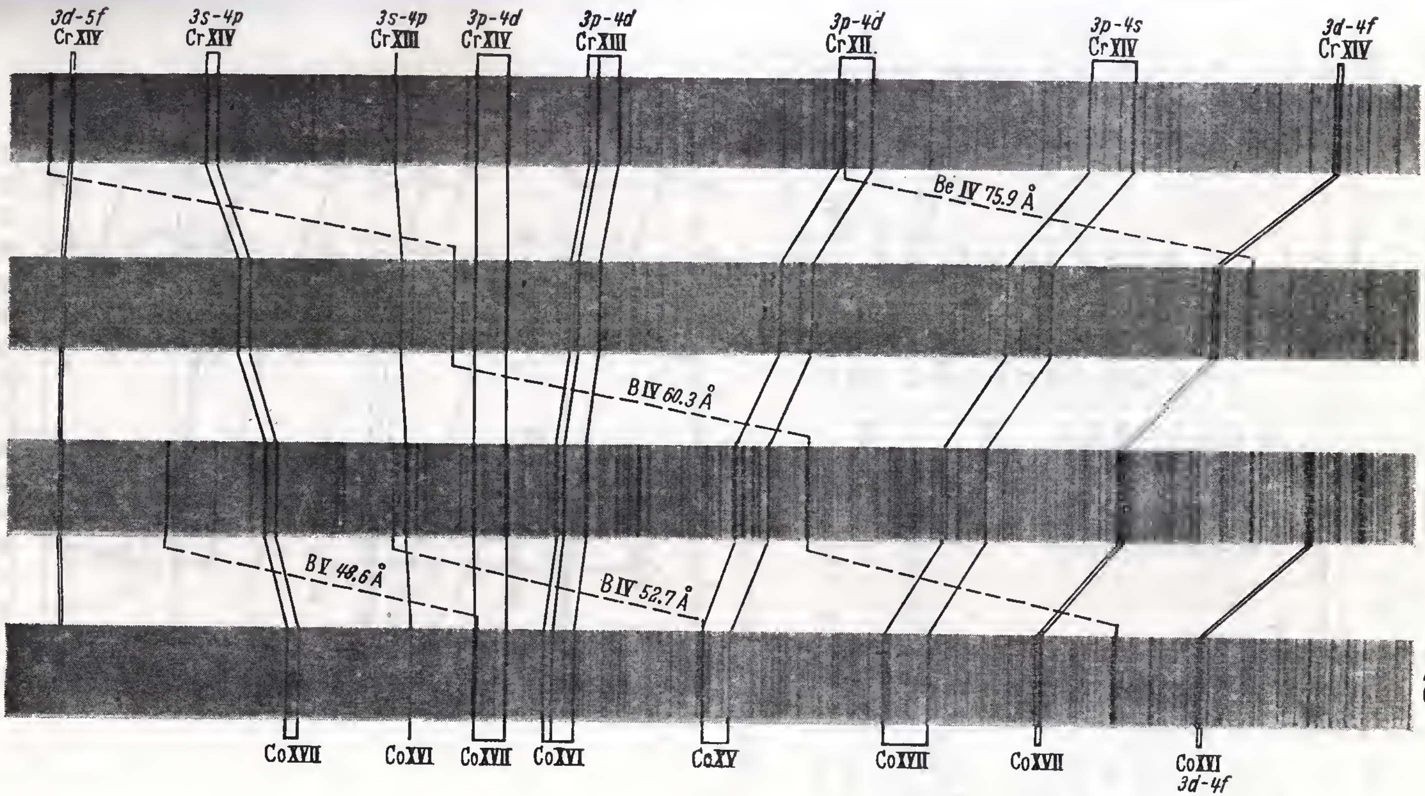



Fig. 7.

Vacuum-spark spectrograms of the region 90 to 40 Å, showing the group of transitions $n = 3$ to $n = 4$ in the Na I-like spectra Cr XIV, Mn XV, Fe XVI, and Co XVII, as well as some lines of the Mg I- and Al I-like spectra of the same elements.

**Table VI.** — *Comparison of the Ground-Term Splittings in the Iso-electronic Sequences* $3s^2 3p$ (Al I, Si II, ...) *and* $3s^2 3p^5$ (Cl I, A II, ...); $\zeta = \frac{2}{3} \Delta\nu$.

| Z | Ion | $^2P_{\frac{3}{2}} - {}^2P_{\frac{1}{2}}$ cm$^{-1}$ | $\sqrt[4]{\zeta}$ | Diff. | Ion | $^2P_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$ cm$^{-1}$ | $\sqrt[4]{\zeta}$ | Diff. |
|---|---|---|---|---|---|---|---|---|
| 13 | Al I | 112.04 | 2.939 | | | | | |
| 14 | Si II | 287.3 | 3.720 | 0.781 | | | | |
| 15 | P III | 559.6 | 4.395 | .675 | | | | |
| 16 | S IV | 950.2 | 5.017 | .622 | | | | |
| 17 | Cl V | 1 492 | 5.616 | .599 | Cl I | 881 | 4.923 | |
| 18 | A VI | 2 210 | 6.195 | .579 | A II | 1 432 | 5.559 | 0.636 |
| 19 | K VII | 3 131 | 6.759 | .564 | K III | 2 162 | 6.162 | .603 |
| 20 | Ca VIII | 4 305 | 7.319 | .560 | Ca IV | 3 115 | 6.751 | .589 |
| 21 | Sc IX | 5 759 | 7.871 | .552 | Sc V | 4 325 | 7.327 | .576 |
| 22 | Ti X | ... | ... | | Ti VI | 5 825 | 7.894 | .567 |
| 23 | V XI | ... | ... | .543 | V VII | 7 657 | 8.452 | .558 |
| 24 | Cr XII | ... | ... | | Cr VIII | ... | ... | |
| 25 | Mn XIII | ... | ... | | Mn IX | ... | ... | .553 |
| 26 | Fe XIV | 18 852.5 (*) (λ 5303) | 10.588 | | Fe X | 15 683.2 (*) (λ 6374) | 10.112 | |
| 27 | Co XV | ... | ... | 0.538 | Co XI | ... | ... | 0.545 |
| 28 | Ni XVI | 27 762 (*) λ 3601) | 11.664 | | Ni XII | 23 626 (*) (λ 4231) | 11.203 | |

(*) Wave-numbers of coronal lines.

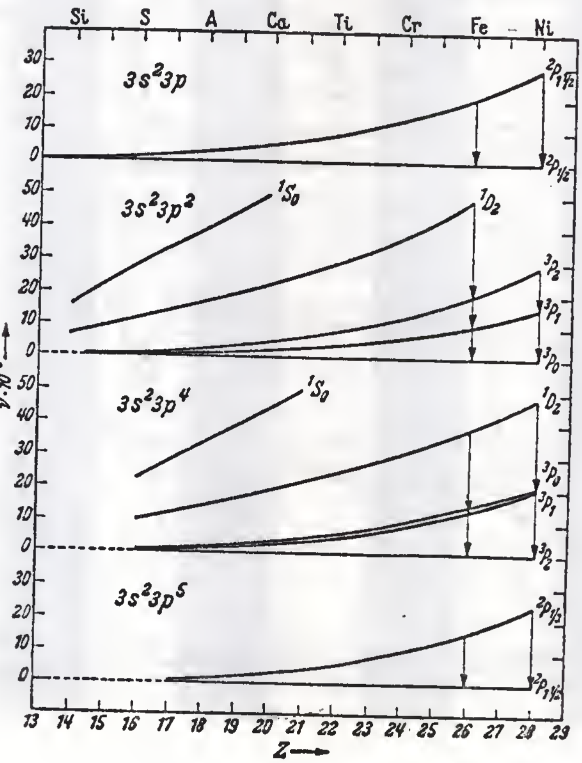
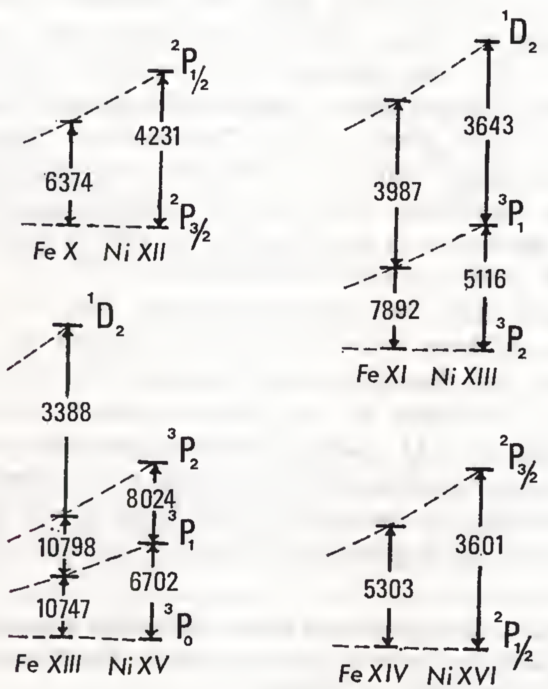


TABLE VII. — $3s^23p^4$ (S I, Cl II, ...).

| Ion | $^3P_1 - {}^3P_2$ | $\sqrt[4]{\zeta}$ | | $^1D_2 - {}^3P_1$ | $F$ cm$^{-1}$ | |
|---|---|---|---|---|---|---|
| S I | 397 | 4.441 | 661 | 8 843 | 7 523 | 1 871 |
| Cl II | 697 | 5.102 | 619 | 10 955 | 9 394 | 1 765 |
| A III | 1 112 | 5.721 | 599 | 12 898 | 11 159 | 1 701 |
| K IV | 1 673 | 6.320 | 582 | 14 713 | 12 860 | 1 657 |
| Ca V | 2 407 | 6.902 | 572 | 16 424 | 14 517 | 1 629 |
| Sc VI | 3 350 | 7.474 | 562 | 18 047 | 16 146 | 1 612 |
| Ti VII | 4 535 | 8.036 | 555 | 19 592 | 17 758 | |
| V VIII | 6 006 | 8.591 | | ... | ... | |
| Cr IX | ... | ... | 550 | ... | ... | 1 580 |
| Mn X | ... | ... | | ... | ... | |
| Fe XI | 12 668 (*) ($\lambda$ 7892) | 10.240 | | 25 075 (*) ($\lambda$ 3987) | 24 079 | |
| Co XII | ... | ... | 543 | ... | ... | 1 538 |
| Ni XIII | 19 541 (*) ($\lambda$ 5116) | 11.326 | | 27 443 (*) ($\lambda$ 3643) | 27 155 | |

(*) From coronal lines.



By studying the $Z$ dependence of the $2s^2\ 2p^5\ {}^2P$ intervals in the F I sequence in the light of new observations, he finds unquestionable confirmation of the coronal identifications: Ca XII at $\lambda$ 3327, Ar X at $\lambda$ 5533.4 and S VIII at $\lambda$ 9911. Similarly, for the $2s^2\ 2p\ {}^2P$ intervals in the B I sequence the new coronal lines give intervals that confirm the identifications as S XII, Si X, Mg VIII and Ar XIV. All of these lines are in highly-ionized spectra of familiar elements.

More significant, however, is Edlén's suggestion that 19 coronal lines heretofore unidentified may well be attributed to transitions from the metastable levels in the configurations $3s^2\ 3p^k\ 3d$ $(k = 3, 4, 5)$ of Fe XI, Fe X, Fe IX and Ni XIII, Ni XII, Ni XI, in the S I, Cl I and Ar I sequences, respectively. This conclusion is based on theoretical calculations giving predicted forbidden wavelengths in the respective sequences. To quote, « none of the metastable levels has yet been located in the relevant ions ». However, by using this theoretical information « we may judge the chances for the configurations $3s^2\ 3p^k\ 3d$ to hold the key to the problem » [14]. Here is another beautiful illustration of important astrophysical work based upon regularities in atomic spectra.

Table VIII gives a summary of atomic lines in spectra of the elements H through Ni identified in the solar spectrum. Roman numerals denote the stage of ionization. The solid circles in the two upper rows indicate familiar spectra whose lines are identified in the Fraunhofer absorption spectrum. Diagonal lines denote spectra that have been identified in the « *XUV* » solar spectrum, i.e., the ultraviolet solar spectrum as observed from rockets and orbiting solar telescopes; these results are quoted mostly from R. Tousey [15] and his associates (1). The solid circles for stages of ionization VIII to XVI indicate the coronal lines produced from forbidden transitions which are the intervals in metastable terms along selected sequences as described above. Two of these entries, Cr IX and Fe XII, are subject to some question.

Several facts stand out in this summary. The top row of figures shows, on a logarithmic scale, the relative abundances of elements in the sun. In 1929 [16] Russell pointed out that with the exception of H, which surpasses all others by far, « the well-known difference between elements of even and odd atomic number is conspicuous — the former averaging ten times as abundant as the latter ». The elements B, F, Na, P, Cl, and especially Co stand out among those of odd atomic number, 5, 9, 11, 15, 17, 27 whose spectra are absent or scarce in Table VIII.

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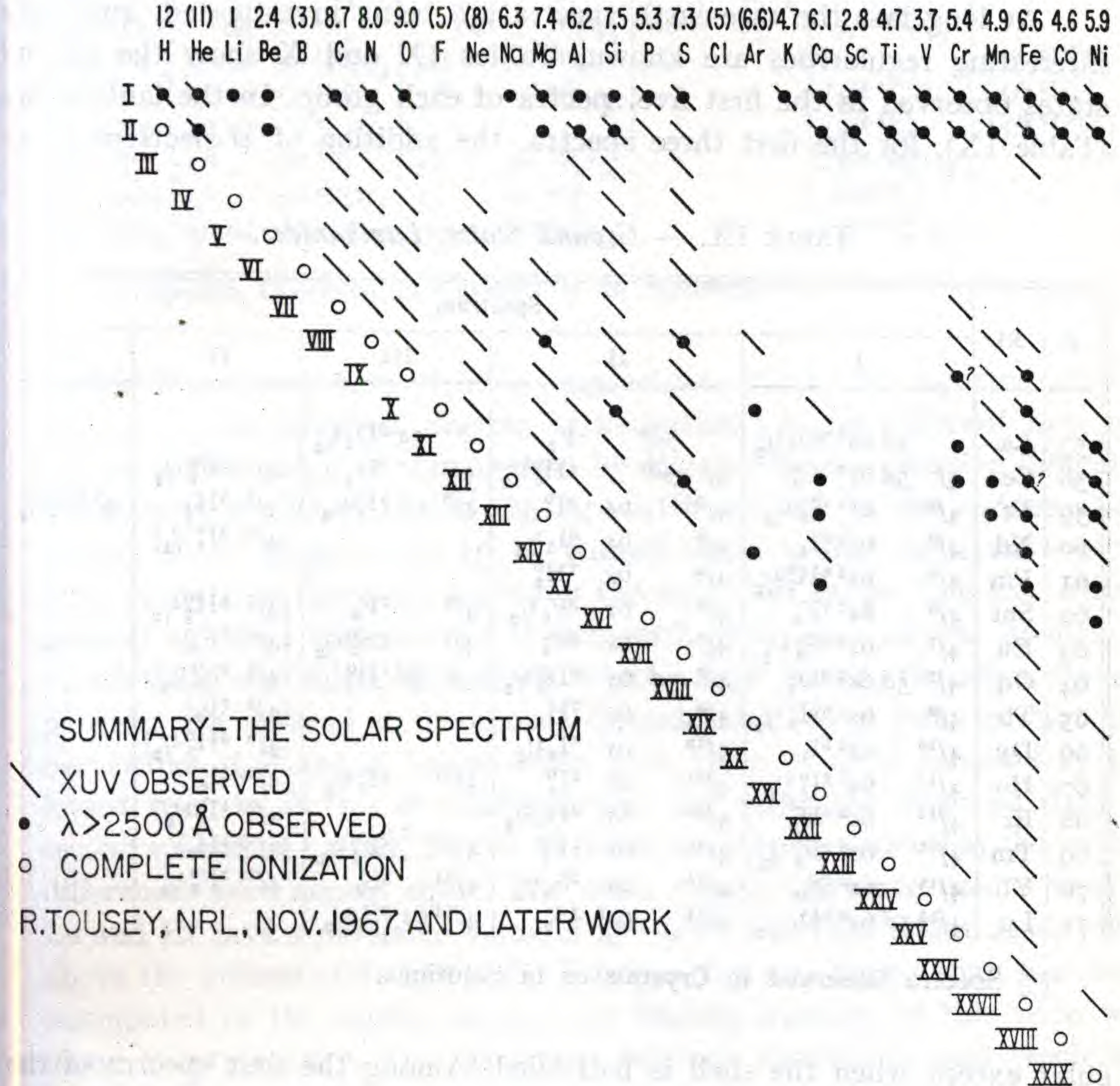
(1) The author has entered Si V and Si VI in Table VIII as identified, on the basis of published material. In a private communication R. Tousey has noted that these identifications require further confirmation.

When more laboratory spectra in intermediate stages of ionization in the first long period have been studied, additional identifications can doubtless be made. Many solar lines still remain unidentified and many laboratory spectra still need to be observed and analyzed.

TABLE VIII.




*Rare-Earth Spectra*: With the completion of volume III of *Atomic Energy Levels* in 1958, the Periodic Table was covered except for the two groups of rare-earth spectra, the lanthanides, Ce through Lu ($Z = 58$-$71$) and the actinides, Th through Lw ($Z = 90$ to $103$). Most of these spectra had not been observed and separated, and regularities were known in comparatively few of them. In the respective groups, the fourteen $4f$- and $5f$-electrons are being built in, and the low configurations overlap. This results in strong combinations in the infrared region. The spectra

are extremely complex and the difficulty in interpreting them is attributable to two factors, described in an excellent paper by Z. B. Goldschmidt [17] as competition between configurations and competition between interactions. « The binding energies of the $4f$-, $5d$-, $6s$- and $6p$-electrons are roughly equal. It may, therefore, be regarded as the manifestation of a basic competition between electrons in these spectra ».

At long last the rare-earth spectra are being investigated, and some interesting regularities are known. Tables IX and X show the ground states observed in the first five spectra of each group. In the lanthanides (Table IX), for the first three spectra, the addition of $4f$-electrons is regular except when the shell is half-filled. Among the first spectra of the actinides (Table X), the competition of the $6d$-electron is prominent, but regularities prevail.

TABLE IX. — *Ground States. Lanthanides.*

| $Z$ | El | Spectrum I | Spectrum II | Spectrum III | Spectrum IV | Spectrum V |
|---|---|---|---|---|---|---|
| 57 | La | $5d\,6s^2\ ^2\mathrm{D}_{1^1/_2}$ | $5d^2\ ^3\mathrm{F}_2$ | $5d\ ^2\mathrm{D}_{1^1/_2}$ | | |
| 58 | Ce | $4f\ 5d\,6s^2\ ^1\mathrm{G}^{\circ}_4$ | $4f\ 5d^2\ ^4\mathrm{H}^{\circ}_{3^1/_2}$ | $4f^2\ ^3\mathrm{H}_4$ | $4f\ ^2\mathrm{F}^{\circ}_{2^1/_2}$ | |
| 59 | Pr | $4f^3\ 6s^2\ ^4\mathrm{I}^{\circ}_{4^1/_2}$ | $4f^3\ 6s\ ^5\mathrm{I}^{\circ}_4$ | $4f^3\ ^4\mathrm{I}^{\circ}_{4^1/_2}$ | $4f^2\ ^3\mathrm{H}_4$ | $4f\ ^2\mathrm{F}^{\circ}_{2^1/_2}$ |
| 60 | Nd | $4f^4\ 6s^2\ ^5\mathrm{I}_4$ | $4f^4\ 6s\ ^6\mathrm{I}_{3^1/_2}$ | | $[4f^3\ ^4\mathrm{I}^{\circ}_{4^1/_2}]$ | |
| 61 | Pm | $4f^5\ 6s^2\ ^6\mathrm{H}^{\circ}_{2^1/_2}$ | $4f^5\ 6s\ ^7\mathrm{H}^{\circ}_2$ | | | |
| 62 | Sm | $4f^6\ 6s^2\ ^7\mathrm{F}_0$ | $4f^6\ 6s\ ^8\mathrm{F}_{0^1/_2}$ | $4f^6\ ^7\mathrm{F}_0$ | $[4f^5\ ^6\mathrm{H}^{\circ}_{2^1/_2}]$ | |
| 63 | Eu | $4f^7\ 6s^2\ ^8\mathrm{S}^{\circ}_{3^1/_2}$ | $4f^7\ 6s\ ^9\mathrm{S}^{\circ}_4$ | $4f^7\ 8\mathrm{S}^{\circ}_{3^1/_2}$ | $[4f^6\ ^7\mathrm{F}_0]$ | |
| 64 | Gd | $4f^7\ 5d\,6s^2\ ^9\mathrm{D}^{\circ}_2$ | $4f^7\ 5d\ 6s\ ^{10}\mathrm{D}^{\circ}_{2^1/_2}$ | $4f^7\ 5d\ ^9\mathrm{D}^{\circ}_2$ | $[4f^7\ ^8\mathrm{S}^{\circ}_{3^1/_2}]$ | |
| 65 | Tb | $4f^9\ 6s^2\ ^6\mathrm{H}^{\circ}_{7^1/_2}$ | $4f^9\ 6s\ ^7\mathrm{H}_8$ | | $[4f^8\ ^7\mathrm{F}_6]$ | |
| 66 | Dy | $4f^{10}\ 6s^2\ ^5\mathrm{I}_8$ | $4f^{10}\ 6s\ ^6\mathrm{I}_{8^1/_2}$ | | $[4f^9\ ^6\mathrm{H}^{\circ}_{7^1/_2}]$ | |
| 67 | Ho | $4f^{11}\ 6s^2\ ^4\mathrm{I}^{\circ}_{7^1/_2}$ | $4f^{11}\ 6s\ ^5\mathrm{I}^{\circ}_8$ | $4f^{11}\ ^4\mathrm{I}^{\circ}_{7^1/_2}$ | $[4f^{10}\ ^5\mathrm{I}_8]$ | |
| 68 | Er | $4f^{12}\ 6s^2\ ^3\mathrm{H}_6$ | $4f^{12}\ 6s\ ^4\mathrm{H}_{6^1/_2}$ | | $[4f^{11}\ ^4\mathrm{I}^{\circ}_{7^1/_2}]$ | |
| 69 | Tm | $4f^{13}\ 6s^2\ ^2\mathrm{F}^{\circ}_{3^1/_2}$ | $4f^{13}\ 6s\ ^3\mathrm{F}^{\circ}_4$ | $4f^{13}\ ^2\mathrm{F}^{\circ}_{3^1/_2}$ | $[4f^{12}\ ^3\mathrm{H}_6]$ | |
| 70 | Yb | $4f^{14}\ 6s^2\ ^1\mathrm{S}_0$ | $4f^{14}\ 6s\ ^2\mathrm{S}_{0^1/_2}$ | $4f^{14}\ ^1\mathrm{S}_0$ | $4f^{13}\ ^2\mathrm{F}^{\circ}_{3^1/_2}$ | |
| 71 | Lu | $4f^{14}\ 5d\,6s^2\ ^2\mathrm{D}_{1^1/_2}$ | $4f^{14}\ 6s^2\ ^1\mathrm{S}_0$ | $4f^{14}\ 6s\ ^2\mathrm{S}_{0^1/_2}$ | | |

[ ] Spectra Observed in Crystals or in Solutions.

In the above discussion, the extrapolation of term intervals along sequences has been mentioned. Nothing has been said, however, about the regularities in spectra found by considering relative positions of the lowest terms of configurations for a fixed degree of ionization, as illustrated by M. A. Catalán, F. Rohrlich and A. G. Shenstone in the configurations $d^n$, $d^{n-1}s$, $d^{n-2}s^2$ [18]. To quote from G. Racah [19] « Their results are represented by functions of $n$ by very broken lines but these

TABLE X. — *Ground States. Actinides.*

| $Z$ | El | Spectrum | | | | |
|---|---|---|---|---|---|---|
| | | I | II | III | IV | V |
| 89 | Ac | $6d\ 7s^2\ {}^2D_1{}^1/_2$ | $7s^2\ {}^1S_0$ | $7s\ {}^2S_0{}^1/_2$ | | |
| 90 | Th | $6d^2\ 7s^2\ {}^3F_2$ | $6d^2\ 7s\ {}^4F_1{}^1/_2$ | $6d^2\ {}^3F_2$ | $5f\ {}^2F^o_2{}^1/_2$ | |
| 91 | Pa | $5f^2\ 6d\ 7s^2\ {}^4K_5{}^1/_2$ | $5f^2\ 7s^2\ {}^3H_4$ | | | $[5f\ {}^2F^o_2{}^1/_2]$ |
| 92 | U | $5f^3\ 6d\ 7s^2\ {}^5L^o_6$ | $5f^3\ 7s^2\ {}^4I^o_4{}^1/_2$ | | $[5f^3\ {}^4I^o_4{}^1/_2]$ | $[5f^2\ {}^3H_4]$ |
| 93 | Np | $5f^4\ 6d\ 7s^2\ {}^6L_5{}^1/_2$ | | | $[5f^4\ {}^5I_4]$ | $[5f^3\ {}^4I^o_4{}^1/_2]$ |
| 94 | Pu | $5f^6\ 7s^2\ {}^7F_0$ | $5f^6\ 7s\ {}^8F_0{}^1/_2$ | | $[5f^5\ {}^6H^o_2{}^1/_2]$ | |
| 95 | Am | $5f^7\ 7s^2\ {}^8S^o_3{}^1/_2$ | $5f^7\ 7s\ {}^9S^o_4$ | | $[5f^6\ {}^7F_0]$ | |
| 96 | Cm | $5f^7\ 6d\ 7s^2\ {}^9D^o_2$ | $5f^7\ 7s^2\ {}^8S^o_3{}^1/_2$ | | $[5f^7\ {}^8S^o_3{}^1/_2]$ | |

[ ] Spectra Observed in Crystals or in Solutions.

broken lines show very striking regularities, which are repeated almost exactly for the different degrees of ionization and for different long periods ». A refinement of this method by Racah solved a puzzling difficulty in the work on Yb II, one of the rare-earth spectra. In the configuration $4f^{14}nd$, W. F. Meggers and H. N. Russell failed to find the elusive $5d\ {}^2D$ term in spite of thorough searching through their earlier line list. Racah pointed out that this was not a rare-earth term, because the $4f$-shell of 14 electrons was filled. The above relationships should, therefore, be applicable. He derived a theoretical formula that took into account the barycenter of P and F terms, when both types of term occurred as the lowest term in $d^{n-1}s$ - $d^n$ configurations. By using the observed data in second spectra of Lu, Hf, Ta and W in the formula he noted that the second differences were almost equal. The same second difference used with Yb, Lu and Hf gave a predicted value of $4f^{14}\ 5d\ {}^2D$ for Yb II about 24500 cm$^{-1}$ above the ground state $4f^{14}\ 5s\ {}^2S$. This position was higher than had been anticipated in the earlier search. The leading member of this term was found at 24332 cm$^{-1}$. The agreement between observation and prediction is excellent.

Further keen insight into rare-earth spectra came from Racah. His beautiful theoretical interpretation of these spectra perhaps had its foundation in Yb II. For nearly 15 years he and Meggers worked together fitting observation and theory step by step. This analysis provides the most complete interpretation of a rare-earth spectrum known to date. Racah stated [19] that « The big problem of the rare-earth spectra is the problem of coupling, because only if the coupling scheme is known is it possible to understand $g$-factors, intensities and selection rules... ». Three

different types of coupling schemes occur in various configurations of Yb II [20]. Within each scheme, however, regularities are evident.

As mentioned above, *LS*-coupling holds for terms whose configurations involve the complete $4f^{14}$ shell of electrons, i.e., for the series of three

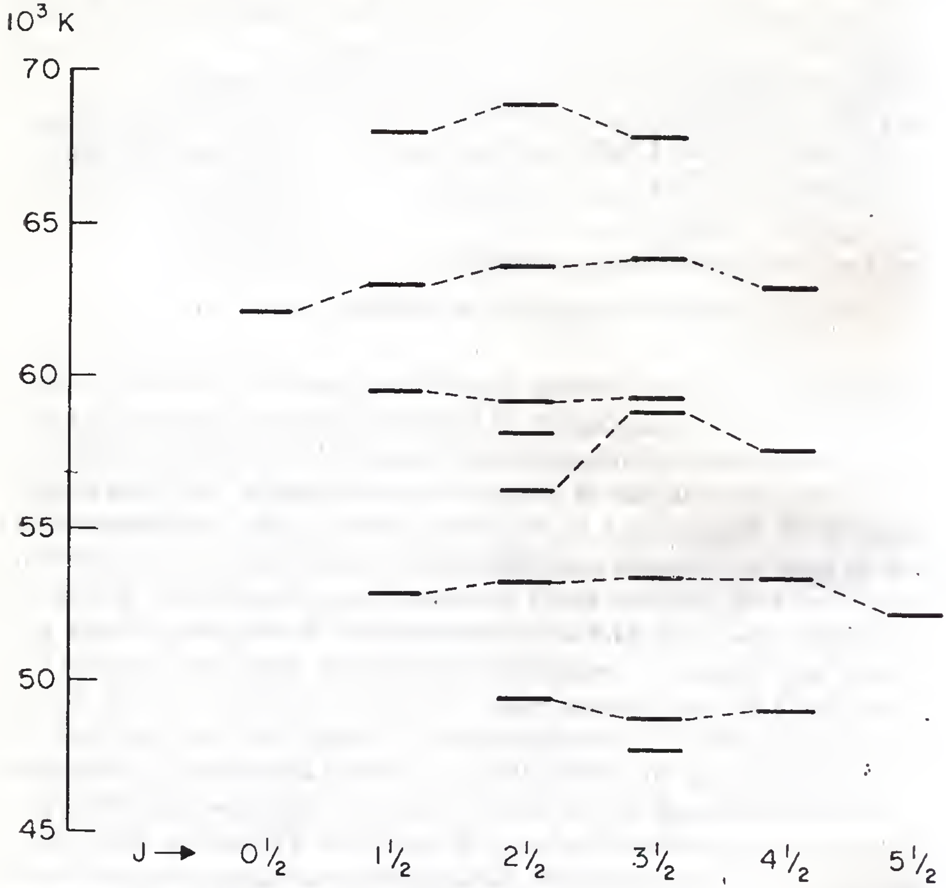



Fig. 8.

The configuration $4f^{13}(^2F^o_{3\,1/2,\,2\,1/2})6s\,6p$ in *Yb* II; $J_I J_{II}$-coupling.

members each $4f^{14}(^1S)ns\ ^2S$ and $nd\ ^2D$, and for the term $4f^{14}(^1S)6p\ ^2P^o$. The same is true for the term $4f^{13}\,6s^2\ ^2F^o$.

Racah first pointed out that limiting terms in the grandparent spectrum (in this case $4f^{13}\ ^2F^o$ in Yb IV) were dominant in rare-earth spectra. He detected, also, an unusual type of coupling, $J_I\,J_{II}$, in the configuration $4f^{13}\,6s\,6p$ in Yb II, [19], [21], a type first noted by A. G. Shenstone in Cu I. In Yb II the low levels are given by three states of $sp\ ^3P_{J_{II}}$: each of these states may assume different orientations in the quadrupole field $f^{13}(^2F_{3\,1/2})$

and thus splits into 1, 3, 5 levels, depending on the $J_{II}$ value. Figure 8 shows the level scheme for both components of the grandparent limit term $^2F^o$, and for $^{3,1}P$. The interval of the ground term $^2F^o$ in Yb IV, 10090 $cm^{-1}$ is clearly effective in Yb II.

The third coupling scheme $J_I L_{II}$ is illustrated in the configuration $4f^{13}(^2F^o)\ 5d\ 6s$ (figure 9). Here the orbital momentum of $5d\ 6s\ ^3D^o$ is

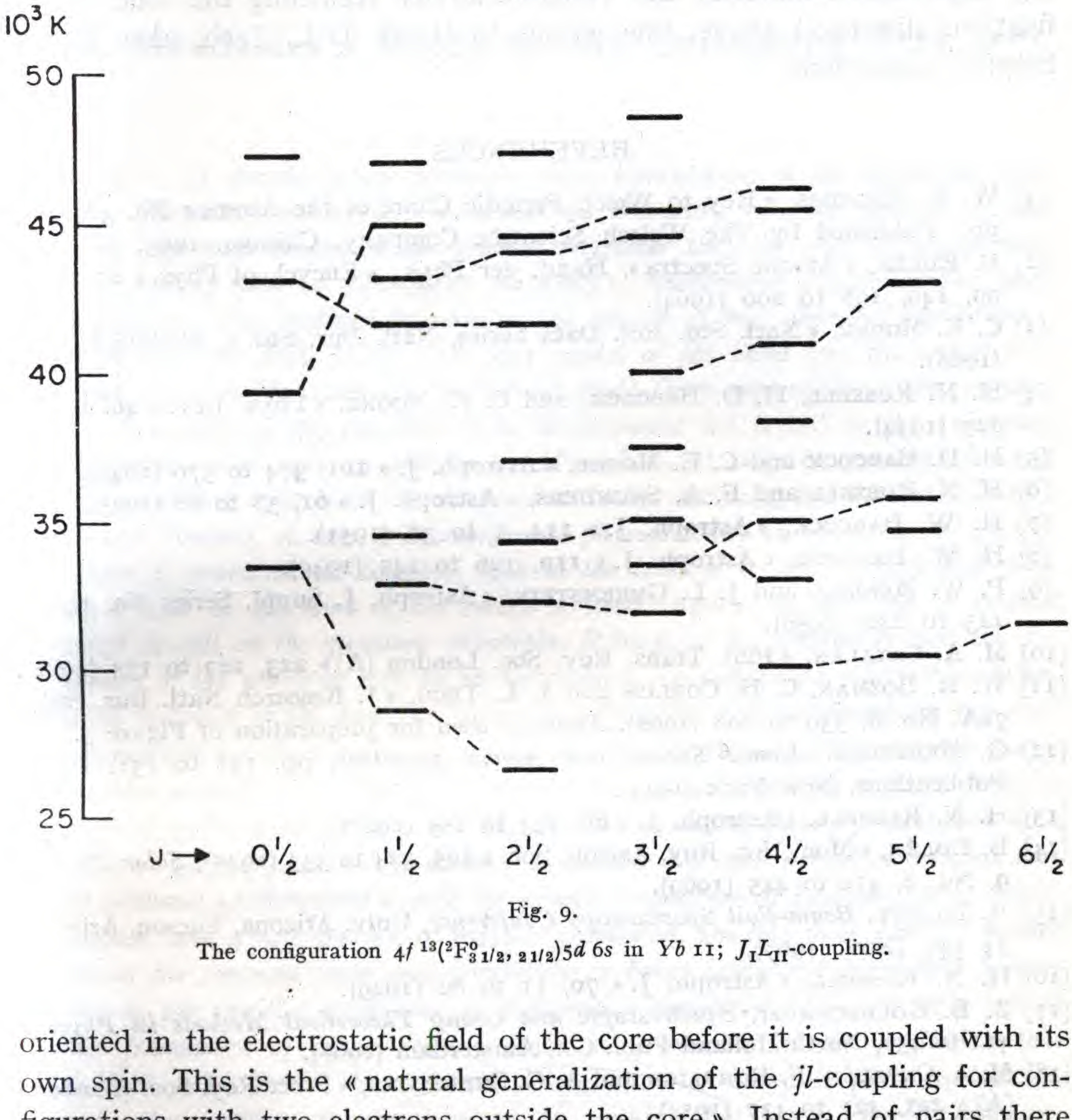



Fig. 9.
The configuration $4f\ ^{13}(^2F^o_{3\ 1/2,\ 2\ 1/2})5d\ 6s$ in *Yb* II; $J_IL_{II}$-coupling.

oriented in the electrostatic field of the core before it is coupled with its own spin. This is the « natural generalization of the $jl$-coupling for configurations with two electrons outside the core ». Instead of pairs there are mostly groups of three levels or isolated levels according to the resultant spin of the outer electrons. Again the interval of the grandparent term is apparent in the figure. Thus, even in these very complex spectra the inherent regularities are a master key to further research.

During the hundred years that have passed since the discovery of the Periodic System of the Elements, atomic spectra have played a ma-

gnificent role. In the century to come our knowledge of Periodicities and Symmetry in the Elementary Structure of Matter will become more and more refined. Future research in atomic spectroscopy will also encompass the unraveling of the mysteries in the intricate spectra of elements having atomic number $Z$ beyond 100.

The writer is deeply indebted to B. Edlén for his generosity in furnishing unpublished material and valuable advice regarding the solar identifications discussed above. She wishes to thank J. L. Tech, also, for his helpful suggestions.

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JOHN ARCHIBALD WHEELER (*)

# From Mendeleev's Atom to the Collapsing Star (**).

**Abstract.** — *A decade before Planck's 1900 formulation of the quantum principle, Mendeleev out of his researches on chemistry and the periodic system of the elements recognized the general character that the new principle must have, dealing with no « deathlike inactivity », establishing « individuality amid continuity », and destined to « hasten the advent of true chemical mechanics ». Implicit in the Bohr-Rutherford 1911 model of the atom was the paradox of atomic collapse. No cheap way out offered itself. Only application of the quantum principle resolved the paradox. This development led (1927) to the « chemical mechanics » envisaged in outline by Mendeleev. It may be symbolized today by an electron orbit with the shape of a double necklace, the « chemical orbit » (Robert Powers). A new crisis confronts physics today in the predicted phenomenon of gravitational collapse, both at the level of a star (« black hole physics ») and at the level of the universe itself. Again no way out is evident except to call on the quantum principle. It leads to the conclusion that the dynamics of the universe goes on in superspace. In superspace alternative dynamical histories of the universe (cycles of expansion and recontraction) not only dynamically couple to each other in the era of collapse, as well as one can judge, but also « coexist ». If the vision of Clifford and Einstein in updated form is taken as guide and particles are regarded as quantum states of excitation of a dynamic geometry, then it is natural to believe that each period of collapse sees the universe « reprocessed », with the previous spectrum of particle masses extinguished, and a new pattern of masses established. On this view particle masses are as far removed from any possibility of being calculated from first principles as the « initial conditions of dynamics » themselves. For an early test of this framework of ideas nothing looks so promising as the prediction that a black hole, formed by whatever combination of baryons, photons, leptons, and other entities, is characterized by nothing but mass, charge, and angular momentum (« transcendence of the law of conservation of baryons and leptons »).*

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## Mendeleev's Goal: Much out of Little.

This centenary of the birth of a great law is also by a coincidence the year of the death of a great architect. Mies van der Rohe expressed the theme of his life work, striving for simplicity and unity, in his famous motto, « Less is more ». What shall be our motto for Dimitri Ivanovich Mendeleev? He sought to the end to see the fantastic wealth of facts of chemistry as consequences of a few central principles. How more briefly can we state this theme than, « Much out of Little »? And if the two worlds of physics and chemistry ever float a flag over their long allied forces, what happier motto could they find for it than *Multum ex parvo*? No words would honor more the cause for which Mendeléev stood.

## Gravitational Collapse: Much into Little.

If « Much out of Little » epitomizes the triumphs of the physical sciences, then also its direct opposite, « Much *into* Little », or « *Multum in parvum* », summarizes the greatest crisis that one can easily name in

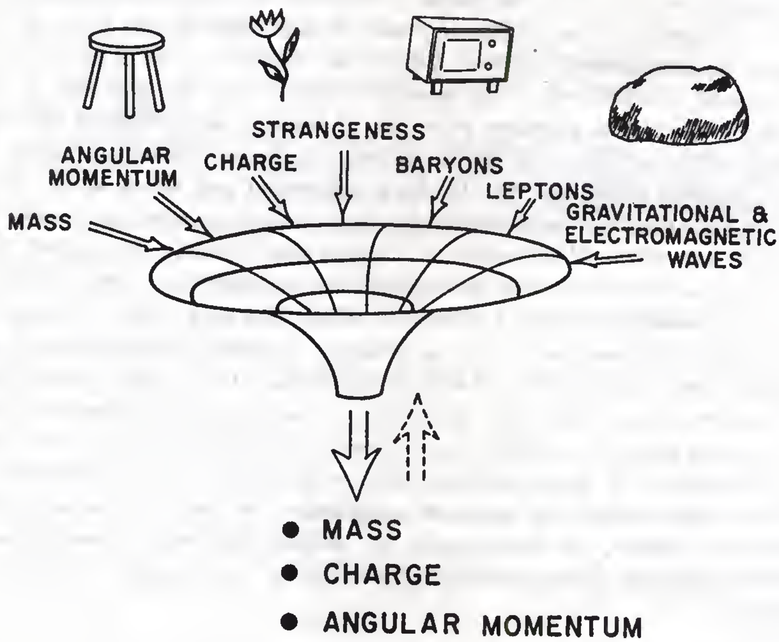


Fig. 1.

« A black hole has no hair ». All particularities of objects dropped in fade away in a characteristic time of less than a millisecond for a black hole of solar mass. No known means whatsoever will distinguish between black holes of the most different provenance if only they have the same mass, charge and angular momentum.

the theoretical physics of our day: to understand what happens in complete gravitational collapse (1).

Fig. 1 illustrates schematically the geometry around a mass, comparable to the sun or greater, that has undergone complete collapse. The details have vanished. The Cheshire Cat in *Alice in Wonderland* also vanished. Only its smile remained behind. What remains behind here? Mass, first of all. This mass binds a planet in orbit as firmly as ever. In addition to mass the collapsed object possesses electric charge and angular momentum (2).

## "A Black Hole Has No Particularities".

The collapse takes place on a characteristic time scale. For an object with a mass comparable to the mass of the sun this time is less than a millisecond. Let the original object have a hill on it. Then the effective height of this hill decreases to half its value in a characteristic relaxation time also less than a millisecond. Dropping to half value, then to quarter value, then to eighth value, and so on, with each stage lasting less than a millisecond, every geographical feature of the system by the end of a second is erased away to the utmost perfection.

Drop in a meteorite. It makes a momentary disturbance in the geometry. It perturbs briefly the centrality of the gravitational attraction

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(1) For an account of gravitational collapse, including a summary of the pioneering contributions of L. D. Landau, S. Chandrasekhar, J. R. Oppenheimer, R. Serber, G. Volkoff, H. Snyder and others, see for example Chapter 6 in B. K. Harrison, K. S. Thorne, M. Wakano and J. A. Wheeler, *Gravitation Theory and Gravitational Collapse*, University of Chicago Press, Chicago 1965; or K. S. Thorne, *Relativistic Stellar Structure and Dynamics*, a section in « High Energy Astrophysics, Proceedings of Course XXXV of the International School of Physics " Enrico Fermi " », L. Gratton, ed., Academic Press, New York 1967, pp. 167-280. For more on many physical and astrophysical issues connected with the topic see Ya. B. Zel'dovich and I. D. Novikov, *Relativistic Astrophysics*, « Esp. Fiz. Nauk » **84**, 377 (1964) and **86**, 447 (1965) [(English translation in « Sov. Physics Uspekhi » **6**, 763 (1965) and **8**, 522 (1966)] and their book on relativistic astrophysics, the English version of which, *Stars and Relativity*, translated by Eli Erlock and edited by K. S. Thorne and W. D. Arnett, is scheduled for 1971 publication by the University of Chicago Press.

(2) The geometry associated with a black hole endowed with angular momentum, an exact solution, like the Schwarzschild geometry, of Einstein's field equations for a region of space (« outside the horizon ») free of all matter, was first reported by R. P. Kerr, « Phys. Rev. Letters », **11**, 237 (1963) and generalized to include charge by E. T. Newman et al., « J. Math. Phys. » **6**, 918 (1965). A detailed analysis of this geometry is given by B. Carter, « Phys. Rev. » **174**, 1559 (1968).

exerted on a planet. That perturbation, that « protruding particularity » also shrinks with time ($\sim lnt/t^7$; R. Price) and fades away. Drop in familiar objects of the greatest variety of sizes and shapes. All details quickly disappear. We end up with an object characterized, so far as we can tell, by mass, charge and angular momentum, and by nothing more. If we call the resulting entity a « black hole », then we can summarize the perfection of its final state by saying, « A black hole has no particularities ».

## Particle Conservation Laws Transcended.

Fire in neutrons, protons, antiprotons, particles and radiations of whatever kind one chooses. In the final object not one of these particularities remains. Make meticulous count of the leptons that one drops in. Check in the baryons with equal care. Compare the resulting black hole with another hole built from a very different number of baryons and leptons. Only require that the two objects have the same mass, charge and angular momentum. Then the one black hole can be distinguished from the other by no known means whatsoever. No measurable meaning of any kind do we know how to give to the baryon number and lepton number of a black hole of unknown provenance (3). Gravitational collapse deprives baryon number and lepton number of all significance.

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(3) The mass of a black hole follows from the period of a test particle in Keplerian orbit around it. The angular momentum follows from the difference in rates of precession of two orbits, one corevolving, the other counterrevolving. The charge follows from an application of the theorem of Gauss. Why should one not then be able to determine still other features of the black hole by still other measurements on test particles outside; and, most immediately, the number of leptons which have collapsed into the black hole by way of the standard ($1/r^5$)-interaction between lepton and lepton (cf. especially G. Feinberg and J. Sucher, « Phys. Rev. » **166**, 1638 (1968) and J. B. Hartle, « Phys. Rev. » **D1**, 394 (1970); note also that the sign reverses when one of the leptons is replaced by its antiparticle!) intermediated by the exchange of two neutrinos? This important question of principle was raised by James B. Hartle in a discussion with the writer at Santa Barbara. Further discussion made it appear reasonable that no influence would remain behind to reveal to the faraway test lepton the lepton number of the particle falling into the black hole. First, there is no Gauss theorem or analogous conservation law that applies to the ($1/r^5$)-interaction. Second, that potential describes an interaction between essentially static leptons, whereas the lepton being captured is in effect fleeing with a speed ever closer to the speed of light. Summer 1970 calculations kindly communicated by Professor Hartle in a preprint of a paper to be submitted by him to « Physical Review » now give a field theoretical analysis showing that the lepton-lepton interaction is extinguished as one of the leptons approaches the horizon of the black hole, and giving a formula for the rate of this extinction.

« Baryon number is conserved » (4). « Lepton number is conserved » (5). Of all principles of physics these familiar conservation laws belong among

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(4) For evidence on the conservation of baryons in elementary particle processes, see F. REINES, C. L. COWAN, Jr., and M. GOLDHABER, « Phys. Rev. » **96**, 1157 (1954); F. REINES, C. L. COWAN, Jr. and H. W. KRUSE, « Phys. Rev. » **109**, 609 (1957); G. N. FLEROV, D. S. KLOCHOV, V. S. SKOBKIN and V. V. TERENTIEV, « Sov. Physics, Doklady » 3, 78 (1958); the review of G. FEINBERG and M. GOLDHABER, *Microscopic Tests of Symmetry Principles*, « U. S. Nat. Acad. Sci., Proc. » **45**, 1301 (1959) and *Experimental Tests of Symmetry Principles*, « Science » **129**, 1285 (1959); and H. S. GURR, W. R. KROPP, F. REINES and B. MEYER, *Experimental test of baryon conservation*, « Phys. Rev. » **158**, 1321 (1967). Appreciation is expressed to Gertrude and Maurice Goldhaber for a 16 June 1970 phone conversation in which they note the new figure of $10^{21}$ yr for the spontaneous fission of $Th^{232}$ (HOLLANDER and KALMAN, *Table of Isotopes*, 6th ed.) enable one to deduce from the 1954 results of Reines, Cowan, and Goldhaber a limit of $10^{23}$ yr for the life of a baryon against an «inconspicuous» mode of disappearance, not very far from the limit set on the life against any conspicuous mode of disappearance. The author is also indebted to Frederick Reines for the following remarks in a 19 June 1970 letter from him regarding the limits that one can place on a «silent process» of baryon disappearance:

« Let us consider two possibilities which together, I believe, give the least restrictive and hence most believable test of baryon conservation to date under terrestrial conditions. Assume that a proton (or a neutron) disappears from a nucleus and the universe in some undefined manner leaving behind a nucleus with a hole in it i. e. missing a proton (or a neutron). No assumption as to the validity of the other conservation laws is made in this view. It is, however, assumed that what is left behind behaves normally.

« In this circumstance, if the original nucleus is a deuteron, the disappearance of a proton would leave a neutron behind. Therefore, detection of a neutron capture pulse in a suitably designed deuterated system could signal the deuteron breakup — or at least set a lower limit for the occurrence of such a process. An experiment of this kind was actually performed at my suggestion by F. Dix at Case Western Reserve University. He obtained a limit $> 3 \times 10^{23}$ yrs (90% confidence level) for the process

$$D \to n + ?$$

« The case of neutron disappearance can be signaled by the radioactivity of the residual nucleus such as

$$\begin{aligned}&C^{12} \to C^{11} + ?\\ &C^{11} \to B^{11} + e^+ + \nu_e \ \ 1.98 \text{ MeV total}\\ &20 \text{ min.}\end{aligned}$$

« Two pieces of data can be used to establish a limit for neutron disappearance $> 10^{20}$ yrs. One is the residual rate seen ($> 1.5$ MeV) in a 500 gallon liquid scintillation detector located in a salt mine. The other is the positron annihilation rate seen in the old Savannah River neutrino experiment where the target was water

$$\begin{aligned}&O^{16} \to O^{15} + ?\\ &O^{15} \to N^{15} + e^+ + \nu_e\\ &2 \text{ min.}\end{aligned}$$

« I believe it possible to significantly improve these limits if one wishes to do so ».

(5) For evidence of the law of conservation of leptons in elementary particle transformations, see M. GOLDHABER, *Weak Interactions: Leptonic Modes - Experi-*

the most firmly established. Yet with gravitational collapse the content of these conservation laws also collapses. The established is disestablished.

Baryon and lepton number have long served as indices to the discreteness of nature. Today their status changes. Their conservation laws, though often useful, cannot be absolute. The distinction between particles and geometry, though often useful, cannot be absolute. Particles that melt into geometry under one set of circumstances surely cannot be resolved from geometry under other extreme conditions. But what? And when? And how? And what is the higher dynamic law that links particles and geometry together into a larger unity? No theory of particles can correctly describe particles that deals only with particles!

Gravitational collapse, *Multum in parvum*, by linking particles with geometry, raises an old issue in a new form. Is nature continuous or is it discrete? Is Plato to be at last the victor, who tells us (6) that all is geometry? Or is Pythagoras again to prove the better prophet, who teaches us (7) that all is number?

## A Walk with Mendeleev.

Troubling about the mystery of gravitational collapse, great issue of our day, turn for a time on this happy anniversary to Mendeleev's life and work. Find ourselves unexpectedly transported to a bright new world, rich with the glitter of the chemistry of hundreds of compounds high and low and thousands of reactions. Walk in the company of this modest and wise man. Partake of insights as relevant to today as yesterday. And come back refreshed at the end for a new look at gravitational collapse.

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*mental*, a report in « 1958 Annual International Conference on High Energy Physics at CERN, Proceedings », pp. 233-250; V. R. Lazarenko, « Usp. Fiz. Nauk » **90**, 601 (1961), English trans. in « Sov. Phys. Uspekhi » **9**, 860 (1967); B. Pontecorvo on neutrino experiments and the problem of conservation of leptonic charge in « Sov. Phys. JETP » **26**, 984 (1968); K. Boher et al. on the conservation of $\mu$-lepton number, « Helv. Phys. Acta » **43**, 111 (1970); and C. Franzinetti, *Experimental limits on the validity of conservation laws in elementary particle physics*, these « Mendeleev Proceedings », 1971.

(6) Plato (428 B. C. - 348 B. C.), *Collected Dialogs*, ed. by Edith Hamilton and Huntingdon Cairns, Bollingen Series LXXI, Bollingen Foundation, New York, p. 1177: « For if the matter were like any of the supervening forms, then whenever any opposite or entirely different nature was stamped upon its surface, it would take the impression badly, because it would intrude its own shape. Wherefore that which is to receive all forms should have no form ».

(7) Pythagoras ($\sim$ 530 B. C.), « all things are numbers ».

Of all the writings of Mendeleev none is more famous than his *Principles of Chemistry* (8), and of all treatises on chemistry none is a greater pleasure to read, nor better suited to attract the uncommitted reader to chemistry. Fresh and new is one's first impression; and fresh and new it is to the end. Never before had the elements of the same group of the periodic table found themselves together in the same chapter: zinc, cadmium and mercury in one; silicon and the other elements of group IV in another; chromium, molybdenum, tungsten and uranium in yet another; and so on. Never was there a guide that one would follow to clay pit or tannery, mine or mill, with more interest in his observations, more profit in his predictions, or more assurance of discoveries along the way.

If Mendeleev shows us all the world and even something of the moon and stars, he nevertheless is more and does more than any guide. He stands for a cause, « unity [amid]... individuality and... apparent diversity » (9). His enthusiasm communicates itself for the mystery hidden in everything around. He is as exciting as the nature he tells us about. He carries in his hand his magic wand, the periodic law:

> « It was in March 1869 that I ventured to lay before the then youthful Russian Chemical Society the ideas upon the same subject which I had expressed in my just written *Principles of Chemistry*...: (1) The elements, if arranged according to... (2) ... (3) ... (8) ... » (10).

We see him touch it to this frozen fact and that, only to make each in turn spring into life and meaning. As we walk on, see new substances and new reactions, and hear him discourse thoughtfully about one and another, we are the more in suspense about where he will next use his magic wand because we sense that he too is all the time pondering this very question. The periodic law: how much of nature does it subsume? Every day to pose this point was every day to find a fresh new face on all creation.

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(8) Dimitri Ivanovitch Mendeleev (Tobolsk, 7 Feb. 1834 – St. Petersburg 20 Jan. 1907), *Principles of Chemistry*, translated from the Russian 5th ed. by George Kamensky, ed. by A. J. Greenaway, in 2 vols., Longmans, Green and Co., London and New York 1891; cited hereafter as PC I or PC II. The first Russian edition dates from 1869.

(9) PC II, p. 407.

(10) Dimitri Ivanovitch Mendeleev, *The Periodic Law of the Chemical Elements*: Faraday lecture delivered before the Fellows of the Chemical Society in the theatre of the Royal Institution on Tuesday, June 4, 1889; reprinted in PC II, pp. 435 ff., and referred to hereafter as FL. The cited passage occurs on p. 436.

## Ten Years from another Uncovering of the Unity Hidden in Diversity.

As we read on in Mendeleev, we suddenly sense that there is something strangely familiar about the man and the message. Whom else have we met equally in love with the richness of the world around? Equally master of it? Equally modest? What other overarching principle, emergent midway on a voyage of discovery, yielded equal thrill to its discoverer? Equal power to find the unity hidden in diversity? Equal radiance so to light up nature that it never looked the same again? And then we remember: Charles Darwin ([12]) and Dimitri Mendeleev; the *Origin of Species* ([13]) and the periodic law. Only twenty years separated the two men in age; and only ten years, their great publications. Each was anticipated by a lesser formulation: Darwin by Alfred Russell Wallace ([14]); Mendeleev by Lothar Mayer ([15]). In each case it was the greater man who understood the new principle the more deeply and made the greater lifetime commitment to testing and applying it. Whether we accompany Darwin on his sand path or join Mendeleev in his lecture hall, we walk with an inspiring companion through a nature suffused with new light and color.

## Homely Facts and Industrial Forecasts.

Mendeleev tells us about the chemistry and mechanics of a running mountain stream and the constitution of the cloudy water. « The coarser particles are first deposited... whilst the clay, owing to its finely divided state, is carried on further, and is only deposited in the still parts of... the estuaries of rivers, lakes, seas, and oceans... A detached account of the theory of falling bodies in liquid, and of the experiments bearing on this subject, may be found in my work, *Concerning the Resistance of Liquids and Aeronautics*, 1880... Thus gold and other heavy ores are washed free from sand and clay... » ([16]). These are homely facts, but they are vital to one who sees the central role of atomic volumes in the esta

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([11]) FL, p. 439.

([12]) Charles Darwin (Shrewsbury, 12 Feb. 1809 - Down, 19 April 1882).

([13]) C. Darwin, *Origin of Species*, 24 Nov. 1859.

([14]) Alfred Russel Wallace (1823-1913), *On the Tendencies of Varieties to depart indefinitely from the Original Type*, Feb. 1858.

([15]) J. Lothar Meyer (1830-1895), *Die modernen Theorien der Chemie*, Breslau 1864.

([16]) PC II, pp. 67-68.

blishment of the periodic system, and who has been concerned with volumes and densities since he was twenty: « [I] occupied myself since the fifties (my dissertation for the degree of M. A. concerned the specific volumes, and is partially printed in the Russian Mining Journal for 1856) with the problems concerning the relations between the specific gravities and volumes, and the chemical composition of substances... » ([17]). From clay he goes on to describe the different kinds of soil and the reasons for their differing suitability for cultivation, and ends by giving detailed analyses of four soils from very different parts of Russia ([18]).

Mendeleev does not finish the chemistry of lead without telling us how white lead is manufactured for paint and how it acquires its covering power ([19]). He explains the inflammability of phosphorous, and the operation of safety methods ([20]). He describes the precautions to be taken in testing for poisoning by arsenic ([21]). In his eyes not one element lacks interesting features, often puzzling features. Mendeleev communicates his omnivorous interest to us, and often gives us his simple explanation for a puzzle. « If a prismatic crystal of sulphur be thrown into one branch of the U tube containing the liquid sulphur at 100°, and an octahedral crystal be thrown into the other branch, then, as Gernez showed, the sulphur in each branch will crystallize in corresponding forms, and both forms are obtained at the same temperature; therefore it is not the influence of the temperature only which causes the molecules of sulphur to distribute themselves in one or another form, but also the influence of the crystalline parts already formed. This phenomenon is essentially analogous to the phenomena of supersaturated solutions » ([22]).

Not only a great investigator, Mendeleev was also a great teacher. To the immense throngs of students who came to his St. Petersburg lectures he gave a new vision of chemistry and at the same time a new view of the future. « There is no doubt that in time the alloys of aluminium will be very widely used... [Aluminium] is distinguished for its capacity to fill up the most minute impressions of the mold into which it may be cast » ([23]). « ... if rich deposits of nickel are discovered a wide field of application lies before them » ([24]). « ... in England alone the annual

([17]) PC II, p. 31.
([18]) PC II, p. 69.
([19]) PC II, p. 135.
([20]) PC II, p. 149.
([21]) PC II, p. 176.
([22]) PC II, p. 198.
([23]) PC II, p. 82.
([24]) PC II, p. 345.

output of cast iron is above 8 million tons, and that of the whole of Europe and America about 15 million tons. Russia contributes but a small part proportionately — namely, about one-fortieth of the whole production — although the Ural, the Don district, and other parts of Russia represent the combination of all advantageous conditions for the future successful development of a vast iron industry» ([25]). «The fuel of blast furnaces consists of wood charcoal..., anthracite (for instance, in Pennsylvania and in Russia at Pastouhoff's works in the Don district), coke, coal, and even wood and peat. It must be borne in mind that the utilization of naphtha and naphtha refuse would probably give very profitable results in metallurgical processes. Here experiments are absolutely necessary, and particularly important for Russia, because the Caucasus is capable of yielding vast quantities of naphtha» ([26]).

## Colleagueship.

If Mendeleev gives, he also receives. He not only listens to the quiet voice of nature, he also seeks out and responds warmly to the best thinking of his colleagues. He cites more than 500 authors in a single volume of his book. For example, referring to the numerical value of atomic weights, he notes, «Ten years earlier such knowledge did not exist, as may be gathered from the fact that in 1860 chemists from all parts of the world met at Karlsruhe in order to come to some agreement, if not with respect to views relating to atoms, at any rate as regards their definite representation. Many of those present probably remember how vain were the hopes of coming to an understanding, and how much ground was gained at that Congress by the followers of the unitary theory so brilliantly represented by Cannizzaro. I vividly remember the impression produced by his speeches, which admitted of no compromise, and seemed to advocate truth itself, based on the conceptions of Avogadro, Gerhardt, and Regnault, which at that time were far from being generally recognized. And though no understanding could be arrived at, yet the objects of the meeting were attained, for the ideas of Cannizzaro proved, after a few years, to be the only ones which could stand criticism, and which represented an atom as — 'the smallest portion of an element which enters into a molecule of its compound'» ([27]).

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([25]) PC II, p. 316.
([26]) PC II, p. 310.
([27]) PC II, p. 327.

## The Periodic Law.

Besides judgment Mendeleev had courage. His bold and clear formulation of the periodic law, as he himself puts it, « by insisting on the necessity for the revision of supposed facts, exposed itself at once to destruction » ([28]). He notes for example, « In my first memoirs... I particularly insisted on the necessity of altering the then accepted atomic weights of cerium, lanthanum and didymium. Cleve, Höglund, Hillebrand, and Norton, and more especially Brauner, and others accepted the proposed alteration, confirmed my determination of the specific heat of cerium, and gave fresh proofs in favour of the proposed alterations of the atomic weights » ([29]). Such examples, numerous though they are, are far from measuring Mendeleev's boldness. Lothar Mayer had made a classification of the known elements, but he had not ventured to predict new elements. Mendeleev did. Eighteen years later (1889) he could say, « We now know three cases of elements whose existence and properties were foreseen by the instrumentality of the periodic law. I need but mention the brilliant discovery of *gallium* [1875], which proved to correspond to ekaaluminium of the periodic law, by Lecog de Boisvaudran; of *scandium* [1879], corresponding to ekaboron, by Nilson; and germanium [1886], which proved to correspond in all respects to ekasilicon, by Winkler. When, in 1871, I described to the Russian Chemical Society the properties [density, valences, chemical activity, etc.], clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery... as a confirmation of the exactitude and generality of the periodic law » ([30]).

Our guide stresses that « even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries » ([31]).

How prophetic! In taking atomic weight as guide to the construction of his table, Mendeleev was operating, we realize today, not with one periodic system, but two: one for the atoms, the other for the nuclei. The one was being played off against the other, a remarkable balancing act. That out of this double puzzle Mendeleev could come to the

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([28]) PC II, p. 439.
([29]) PC II, p. 89.
([30]) PC II, p. 447.
([31]) PC II, p. 447.

correct order of the elements and reach within an ace of the concept of atomic number is a tribute in part to the relatively simple course of the valley of stability (32) in the chart of the nuclei. It is more; it is a tribute to Mendeleev's insight and judgment.

## The Quantum Principle before the Quantum Principle.

The periodic law to Dimitri Ivanovitch was not the end of chemical science, but the beginning; it was a clue to the central mystery: the machinery of matter. Ask him to spare a few steps more with us to tell us of his reflections on this mystery. He replies that he cannot accept a static model of a molecule, nor follow chemists who « represent... the interior of molecules... as being in a condition of death-like inactivity » (33). It may or may not be true that « our atoms may... be compared to... solar systems » (34); but to him, « The conviction that motion pervaded all things... has now extended to the unseen world of atoms » (35). We must « harmonize... chemical theories with the immortal principles of Newtonian natural philosophy, and so hasten the advent of true chemical mechanics » (36).

« Hasten the advent of true chemical mechanics ». The words come just as our guide is saying farewell. We hold him a minute more. « A new mechanics inside an atom! What an inspiring thought! How you must have pondered this vision! Can you spare a last word on the central feature of this newness? ». Mendeleev turns from eyes to the distance, stands a time silently, then slowly frames his great reply: « ... while we admit... throughout the universe a unity of plan, a unity of forces, and a unity of matter... we none the less must explain the individuality and the apparent diversity which we cannot fail to trace everywhere. ... After a long and painstaking research, natural science has discovered the individualities of the chemical elements ... Unity and the general, like time and space, like force and motion, vary uniformly. The uniform admit of interpellations, revealing every intermediate phase; but the multitudinous, the individualized — ..., like the chemical elements, ..., like Dalton's multiple proportions — [are] characterized in another way. We see... — side by side with general connecting principle — leaps, breaks

(32) « Valley of stability » in G. Gamow, *Structure of Atomic Nuclei and Nuclear Transformations*, Oxford University Press, 1937.
(33) PC II, p. 418.
(34) PC II, p. 418.
(35) PC II, p. 417.
(36) PC II, p. 419.

of continuity, points which escape from the analysis of the infinitely small — a complete absence of intermediate links. However, the place for individuality is... limited by the all-grasping, all-powerful universal... » (37). And then he vanishes. This is Mendeleev, in 1889 revealing to us the nature of the quantum principle, eleven years before the discovery of the quantum principle! No one came close to being so good a prophet.

Our edition of Mendeleev's book appeared in 1891, at the beginning of the « great decade »: 1895, x-rays; 1896, radioactivity; 1897, the electron; and 1900, the quantum. Turn back in the volume that he left behind to this passage: « The alteration or doubling of the atomic weight of uranium — *i.e.*, the recognition of U = 240 — was made for the first time in the first (Russian) edition of this work (1871), ..., because with an atomic weight 120 [the value previously generally accepted by chemists], uranium could not be placed in the periodic system » (38). Read later in the book that now « its high atomic weight is received without objection, and it endows that element with special interest » (39). And as if Mendeleev himself were staging the surprises to come, read his note, « Becquerel, Bolton and Morton have made some most interesting researches on the phosphorescent spectra of the uranium compounds... » (40).

## Nuclear Physics Opening up Atomic Physics.

We known the story (41): Henri Poincaré and A. H. Becquerel sitting together at a session of the Paris Academy, discussing like everyone else at the time the mystery of the rays discovered by Konrad Roentgen; the remark of Poincaré to the effect, you have seen and told us in the past about strange radiations from uranium; his query, would it not be worthwhile to see if uranium produces anything like Roentgen's rays; and the sequel: Becquerel's wonderful discovery (42).

(37) PC II, pp. 407-408.
(38) PC II, p. 287.
(39) PC II, p. 449.
(40) PC II, p. 288.
(41) I owe the story to the kindness of Professor Gorodetsky of the University of Strassbourg at Warsaw 17 October 1967 who tells me that he heard it in turn from the son of Becquerel. Another part of the story recounts the admiration that the elder Becquerel expressed on his return from London to Paris for the then very young Rutherford, « Il y a en Angleterre un jeun homme qui devine tout ».
(42) H. A. Becquerel, « Acad. Sci. Paris, Compt. rend. », pp. 122, 420, 501, 559, 689, 762, 1086 (1896).

From 1896 and radioactivity to 1926 and the « true chemical mechanics » envisaged by Mendeleev was an unplanned voyage of discovery, a zig-zag journey from paradox to paradox.

Radioactivity itself was a double paradox. Belying any small vision of « deathlike inactivity » in the atom, it inaugurated a « nuclear chemistry » that burst the bounds of molecular chemistry and outdid it in energy by six orders of magnitude. Paradox No. 1: Products of nuclear radioactivity had to be scattered by the nucleus to reveal the planetary structure of the atom. Paradox No. 2: The completely probabilistic character of elementary quantum jumps revealed itself in nuclear transformations a decade sooner than in atomic transitions. The planetary structure plus Earnshaw's theorem, no stable equilibrium for any static system of point charges, led to paradox No. 3: Why do not solids and liquids collapse in $10^{-10}$ sec? Once confronted by the prediction that all matter should collapse, one had no cheap way out, any more than one has today any evident escape from the issue of gravitational collapse. Collapse was the crisis of 1910 as collapse is again the crisis of 1970.

Don't give up Coulomb's law of force between charged particles. Don't deny that an accelerated charge radiates. Accept instead the consequences of the inescapable quantum of Planck for the motion of an electron in an atom. With this daring conservatism Bohr resolved the crisis of « atomic collapse » and opened the door to the understanding of atomic structure. However, molecular structure remained a mystery pending a still deeper elucidation of the quantum principle.

## Electron Orbits and Chemical Bonds.

Many there were in the early 1920's who could not believe that the tetrahedral valences of carbon had the slightest connection with the circular and elliptic orbits of Bohr; and many were deeply convinced that chemistry is chemistry and physics in physics: that chemical forces are chemical forces and electrical forces are electrical forces.

Superpose *s*- and *p*-state wave functions to built quantum states of directed valence! That was the key of Heitler and London (43) to unlock the central mystery of chemistry. This idea in its rich unfolding and consequences (44) gave the world at last Mendeleev's « true chemical

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(43) W. Heitler and F. London, « Zeits. f. Physik » 44, 455 (1927) and later papers.

(44) See for example L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 3rd ed., 1960.

mechanics ». In one way this development was an anticlimax. There was no new force hidden in chemistry, nor any new principle. Something so « accidental » as the near identity in energy of two quantum states allowed the building of a directed probability wave. At issue in producing this degeneracy was only the modicum of energy of binding of the last electrons. The appetite of the atomic field for negative charge had been almost satiated before this point was reached. « Tiny residuals » was the final diagnosis of « chemical forces » as compared to atomic binding. Little surprise there was at the end that homopolar bonds should differ in strength by orders of magnitude from Van der Waals couplings.

In another sense « directed valence » was the climax of four decades of elucidation of the quantum principle. If Darwin reduced the richness of life to the principle of natural selection, the quantum principle reduced the richness of solids, liquids, and gases, and of all chemistry, to the dynamics of a collection of moving point charges ([45]). In no way was it required or right to meet each complication of physics or chemistry with a corresponding complication of principle. One had emerged into a world of light, where nothing but simplicity and unity was to be seen. If sovereign light extended its rule so far by capitalizing on the crisis of atomic collapse, how can it fail to seize the crisis of gravitational collapse as opportunity to add elementary particles and the universe itself to its destined empire?

One cannot leave the atom without taking a moment to contrast it with the nucleus. In the nucleus the energy of an individual particle is approximately $E = \left(2n_r + l + \frac{3}{2}\right)\hbar\omega$. Moreover the effective potential approaches more closely the assumed ideal harmonic potential, $V = \frac{1}{2} m\omega^2 r^2$, as the number of particles increases. In contrast, in the same many-particle limit the atomic potential in the bulk of the atom deviates more and more widely from the simple Coulomb law, $V = - Ze^2/r$. The energy levels do not follow the elementary formula $E = - m(Z^2e^4/2\hbar^2)(n_r + l + 1)^{-2}$. Thus in $_{55}$Cs, $_{56}$Ba, $_{57}$La and the lan-

([45]) P. A. M. Dirac in *The quantum mechanics of many-electron systems*, « Roy. Soc. London, Proc. » A123, 714 (1929) writes, « The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble ».

thanide series (ends at $Z = 71$), the $5d$ and $4f$ levels have nearly the same energy (Table I):

Table I.

*d- and f-levels of the same value $k = n + l = n_r + 2l + 1 = 7$ have nearly the same energy for atomic numbers of the order of $Z = 60$.*

| Orbit | $n$ | $n_r$ | $l$ | $k = n + l$ |
|---|---|---|---|---|
| $5d$ | 5 | 2 | 2 | 7 |
| $4f$ | 4 | 0 | 3 | 7 |

## The "Chemical Orbit".

The energy of an outer electron is governed neither by $2n_r + l$ nor by $n_r + l$ but in a certain approximation and over a certain range by $K = n + l = n_r + 2l + 1$; and not only in this region of Mendeléev's table, but also, as has long been known ([46]), in other stages of the level-

([46]) For a quick survey, see for example L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, Oxford 1958, p. 235, p. 245, or E. U. Condon, chapter on *Quantum Mechanics and Atomic Structure*, pp. 7-22, in E. U. Condon and H. Odishaw, eds., *Handbook of Physics*, McGraw-Hill, New York, 2nd ed., 1967. For his pioneering 1926 correlation between the order of shell-filling and $k = n + 1$, see the early reference to Madelung on p. 670 in S. A. Goudsmit and P. I. Richards, « U. S. Nat. Acad. Sci., Proe., » **51**, 664 (1964), who also stress this correlation; see also E. Madelung (himself), *Die mathematischen Hilfsmittel des Physikers*, Springer, Berlin 1950, p. 611 (these references from E. Neubert, kind personal communication and « Zeits. f. Naturforschung » 25 *a*, 210, 1970). For fuller references to the literature on the theory of shell filling see A. Sommerfeld, *Wave Mechanics*, Vol. II, 1933; Yeou Ta, « Ann. Physik » **1**, 88 (1946); L. Simmons, « J. Chem. Ed. » **24**, 588 (1947); R. Hakala, « J. Phys. Chem. » **56**, 178 (1952); V. M. Klechkovski, « Dokl. Akad. Nauk SSSR » **80**, 603 (1951), **86**, 691 (1952), **92**, 923 (1953), and **135**, 655 (1960); also « Zh. Fiz. Khim. » **27**, 1251 (1953) and « Zh. Eksp. teor. Fiz. » **25**, 179 (1953); V. I. Goldanskii, « J. Chem. Educ. » **47**, 406 (1970). For the order of filling of levels as given in the Fermi-Thomas statistical atom model (cf. for example the treatise P. Gombas, *Die statistische Theorie des Atoms und ihre Anwendungen*, Springer, Vienna 1949) see A. Sommerfeld, *Atombau und Spektrallinien, Wellenmechanischer Ergänzungsband*; M. G. Mayer, « Phys. Rev. » **60**, 184 (1941); D. Ivanenko and S. Larin, « Dokl. Akad. Nauk SSSR » **88**, 45 (1953); V. M. Klechkovskii, « Doklady Akad. Nauk SSSR » **92**, 923 (1953), « Zh. Eksp. teor. Fiz. » **26**, 760 (1954); **30**, 199 (1956), English translation in « Soviet Phys. JETP » **3**, 125 (1956); R. Latter, « Phys. Rev. » **99**, 510 (1955); T. Tietz, « Ann. Physik » **15**, 186 (1955) and **5**, 237 (1960); and V. M. Klechkovskii, « Zh. Eksp. teor. Fiz. » **41**, 465 (1961); English translation in « Soviet Phys. JETP » **14**, 334 (1962).

filling process (from $_{48}$Cd through $_{54}$Xe, comparable energies for $4d$ and $5p$ with $k = n_r + 2l + 1 = 7$; and comparable energies for $6d$ and $5f$ with $k = n_r + 2l + 1 = 9$ in a significant part of the range $_{87}$Fr, $_{88}$Ra, $_{89}$Ac and the actinide series; similary earlier in Mendeleev's table). It is known that no other local potential admits a level degeneracy so extreme as one finds for the Coulomb and oscillator potentials (47). Therefore the energy of the electron cannot depend exclusively upon $k = n_r + 2l + 1$ over the full range of orbits (48). What kind of power

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(47) For some of the analysis of potentials in which a particle has energy levels of high degeneracy, see W. LENZ, « Z. Physik » **24**, 197 (1924); V. A. FOCK, « Z. Physik » **98**, 145 (1935); D. I. FIVEL, *Solutions of Scattering and Bound State Problems by Construction of Approximate Dynamical Symmetries*, University of Maryland Technical Report No. 460, May 1965; H. BACRY, H. RUEGG and J. M. SOURIAU, « Comm. Math. Phys. » **3**, 323 (1966); R. HERMANN, *Lie Groups for Physicists*, W. A. Benjamin, New York 1966; P. B. GUEST and A. BØRS, « Proc. Phys. Soc. » **92**, 525 (1967); and J. S. ALPHER and O. SINANOĞLU, « Phys. Rev. » **177**, 77 (1969).

(48) Note on quantum defect and chemical orbit. At the conclusion of this report Emilio Segré raised with the writer the question whether out of the formula often employed in spectroscopy for the correlation of atomic energy levels, $E = -R/(n - \Delta)^2$, one can read out under appropriate circumstances a constancy of $E$ with $l$ for fixed $n + l = n_r + 2l + 1$. The answer turns out to be yes for even one of the simplest and oldest of the models of how effective atomic field increases in strength as the electron reaches deeper into the atom: $V_{eff}(r) = -e^2/r - B\hbar^2/2mr^2$. Here for a certain range of quantum states one takes $B$ to be an appropriately chosen constant. The added term is equivalent in its consequences to a decrease of the coefficient in the repulsive potential of the centrifugal force from $l(l + 1)$ to $l^*(l^* + 1) = l(l + 1) - B$. Add $\frac{1}{4}$ to both sides of this equation and take the root. In this way find that the Rydberg formula undergoes the transformation $E = -R\Big/\left(n_r + \frac{1}{2} + l + \frac{1}{2}\right)^2$

$$\to E = -R\Big/\left(n_r + \frac{1}{2} + l^* + \frac{1}{2}\right)^2 = -R\Big/\left(n_r + \frac{1}{2} + l + \frac{1}{2} - \Delta_l\right)^2.$$

In this model the familiar calculated quantum defect is $\Delta_l = \left(l + \frac{1}{2}\right) - \left[\left(l + \frac{1}{2}\right)^2 - B\right]^{1/2}$. Identical energy for two states means identical corrected Rydberg denominator. If in a certain range of atomic number the $5d$ and $4f$ states are to have nearly the same energy, then the difference between the values of $n = n_r + l + 1$ for those two states, $n_d - n_f = 5 - 4 = 1$, must be compensated by the difference in quantum defects, $\Delta_d - \Delta_f = 1$. This requirement leads to the equation $[5/2 - (25/4 - B)^{1/2}] - [7/2 - (49/4 - B)^{1/2}] = 1$. From it one finds $B = 6$ for the states in question and for the range of atomic numbers in question (formula meaningless for $s$ and $p$ states for this $B$ value!). The calculated individual quantum defects in the example are $\Delta_d = 2.0$, $\Delta_f = 1.0$. For a brief account of empirical

law potential will make the energy depend upon this particular combination of $n_r$ and $l$ for a limited range of orbits has been analyzed in

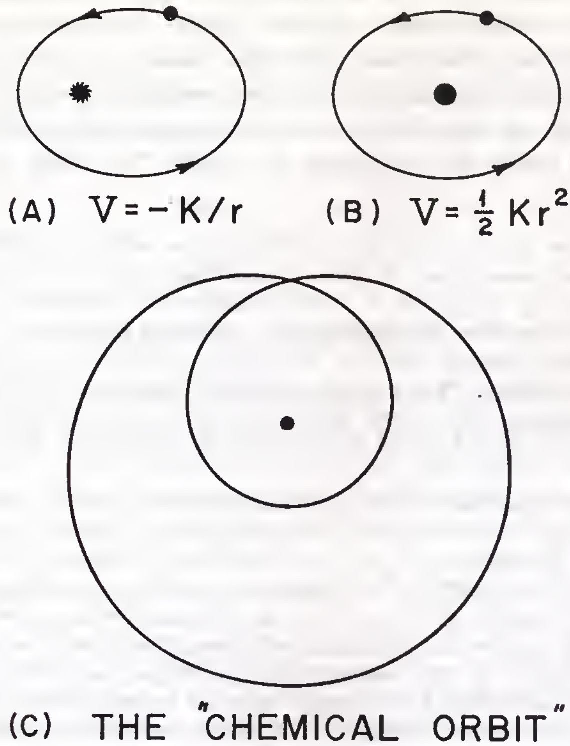


Fig. 2.

(*a*) Kepler orbit. The periods of revolution and of excursion of the radial distance are identical, regardless of the ellipticity of the orbit (« degeneracy of states of the same $n = n_r + l + 1$"). - (*b*) Harmonic oscillator orbit. Two complete radial oscillations in the course of one revolution (« degeneracy of states of the same $2n_r + l$"). - (*c*) Double necklace or « chemical orbit ». One complete radial oscillation in the course of two revolutions (energy dependent upon $n_r + 2l$).

detail by Robert Powers. He also determines the classical orbits themselves. They are very different for the conditions under discussion here

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data on quantum defects and screening constants, see for example E. U. Condon and H. Odishaw, eds., *Handbook of Physics*, McGraw-Hill, New York 2nd ed., 1967, Table 2.2 on p. 7-40 in the chapter by J. R. McNally, Jr., *Atomic Spectra* and Table 8.2 on p. 7-129 and Fig. 8.1 on pp. 7-130 in the chapter of E. U. Condon, *X Rays*, and for more see especially C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467, U. S. Government Printing Office, Washington, D. C., 1949; and S. T. Manson, *Dependence of the Phase Shift on Energy and Atomic Numbers for Electron Scattering by Atomic Fields*, « Phys. Rev. » **182**, 97 (1969), Table I. Appreciation is expressed to Ugo Fano for reference to this last work.

from what they are either for the harmonic oscillator potential or the Coulomb potential (Fig. 2 and Table II).

TABLE II.

*« Chemical orbit » compared and contrasted with orbits in Coulomb potential and simple harmonic oscillator potential.*

| Potential | Orbit | Features of orbit preserved over entire semiclassical range of $n_r$ and $l$? | Reaches $r_{max}$ how many times per circuit of the orbit? | Passes $\theta = 0°$ how many times per circuit of the orbit? |
|---|---|---|---|---|
| Oscillator | Centered ellipse | Yes | 2 | 1 |
| Coulomb | Kepler ellipse | Yes | 1 | 1 |
| Atom | « Chemical orbit » | Restricted range | 1 | 2 |

It follows from the equation

$$E = E(k) = E(n_r + 2l + 1)$$

that the circular frequency of revolution in the classical approximation is twice the frequency of excursions in the radial direction,

$$\omega_r = \frac{\partial E}{\hbar \partial n_r} = \frac{E'}{\hbar} .$$

In other words, the electron, as treated in the semiclassical approximation, must make two complete revolutions to go from perihelion to perihelion: one revolution to go from perihelion to aphelion, and another to go back from aphelion to perihelion (Fig. 2). The orbit has the character of a double necklace. Robert Powers and the writer join in calling this the « chemical orbit ».

Naturally, no single quantum state ever gives a distribution of probability amplitude like that predicted in the classical chemical orbit. For a semiclassical description of motion in an orbit in the spirit of the correspondence principle, one requires a wave packet. To form the required wave packet we superpose quantum states which have very nearly the same energy, $E$, by virtue of having the same $k$ value, but values of $l$ differing by one unit:

$$\psi(r, \theta, \varphi, t) \simeq [u_{L, n_r}(r) (\sin \theta)^L e^{iL\varphi} + u_{L-1, n_r-2}(r) (\sin \theta)^{L-1} e^{i(1-1)\varphi}] e^{-iEt/\hbar} .$$

What requirements must a point of observation fulfill if it is to maximize this probability amplitude? First, $\sin\theta$ must be as large as possible ($\theta = \pi/2$; equatorial plane; this special orientation for orbit chosen for simplicity of analysis), Second, the remaining factors inside the square bracket should have the same phase (constructive interference!). Specifically each radial wave function can be viewed as a standing wave, the linear superposition of an outgoing wave and an incoming wave. The standard JWKB approximation gives for the phase of the outgoing wave

$$\int^r [(2m/\hbar^2)(E - V(r)) - L^2/r^2]^{1/2} dr + L\varphi ,$$

apart from an additive phase constant, irrelevant in the present analysis. Constructive interference between two such outgoing waves with angular momentum quantum numbers $L$ and $L - 1$ does not demand that the phase of either wave individually should be zero. It demands instead that the difference in the phases should vanish at the point of observation. This requirement becomes

$$\int^r \frac{L dr/r^2}{[(2m/\hbar^2)(E - V(r)) - L^2/r^2]^{1/2}} = \varphi$$

where we have replaced the first difference by the derivative evaluated for an angular momentum halfway between $L$ and $L - 1$. We have here the location of the point of constructive interference. The formula just derived is identical with that contained in classical mechanics for the track of the particle in its double necklace orbit. The special feature that distinguishes the chemical orbit from other orbits is the fact that $\varphi$ increases by $2\pi$ as $r$ runs from perihelion to aphelion. Thus we have to deal with the left hand side of (1) considered as a definite integral between the two turning points (defined by the vanishing of the denominator). However, this definite integral, divided by $\pi$, gives according to classical theory exactly the ratio of the fundamental frequencies for revolution and for excursions of the radius. In summary, the conditions encountered in segments of the periodic table, where orbits of the same $k$ value are filled nearly simultaneously, besides being conditions favorable for formation of states of directed valence, are also conditions favorable for the formation of a wave packet that realizes approximately the chemical orbit, in the sense of Fig. 2. A closer analysis shows that there can be two ranges of $r$ values where such motions can occur, separated by a barrier. Moreover, «electron leakage»

can take place through this barrier [49]. So much can one easily do

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[49] Note on « electron leakage » as a periodic phenomenon yet to be observed: Periodic variation with atomic number as it shows itself in chemical binding and directions of valence bonds is not the only type of periodicity. Ionization potentials also vary periodically. So does the calculated cross section (1) for scattering of low energy electrons (data of Ramsauer and Kollath and others, and quantum mechanical interpretation thereof, as summarized in N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, Oxford University Press, London, 3rd ed., 1965; see also L. B. Robinson on Ramsauer resonances in the Fermi-Thomas atom model, « Phys. Rev. » **117**, 128 (1960) and S. T. Manson, « Phys. Rev. » **182**, 97 (1969) and (2) for absorption of light by an inner electron of an atom (U. Fano and J. W. Cooper, cited in the following reference). In this connections A. R. P. Rau and Ugo Fano (« Phys. Rev. » **167**, 7, 1968) emphasize, and give data to support the conclusions that, « properties that depend primarily on *different layers* of the atomic structure are seen to attain extreme values at *different columns* of the periodic table ». One of the most interesting of effects is the double minimum in the effective potential experienced by an electron of angular momentum $l = 3$ (and other $l$ values). At the outer minimum the Coulomb attraction of the almost fully screened nucleus dominates. At the barrier separating the two minima the centrifugal potential dominates. At the inner minimum the attraction of the almost unscreened nucleus dominates. The barrier is predicted by the elementary Fermi-Thomas atom model [E. Fermi in *Quantentheorie und Chemie*, Leipziger Vorträge, ed. by H. Falkenhagen, S. Hirzel Verlag, Leipzig 1928, p. 95, reprinted in *Collected Papers of Enrico Fermi*, University of Chicago Press, Chicago 1962, p. 291; M. Goeppert-Mayer, « Phys. Rev. » **60**, 184 (1941); R. Latter, « Phys. Rev. » **99**, 510 (1955); and further works cited in reference 1 of the paper of R. T. Powers, « Mendeleev Proceding », 1970] to vary smoothly with atomic number, Z. In contrast, Rau and Fano point out, « the height and the very existence of the barrier depend upon Z nonmonotonically... [and] maximum barrier heights occur for Cu, Ag (or Pd) and Au ». This barrier powerfully influences the scattering of slow electrons and the absorption of light by inner electrons, as emphasized by Rau and Fano, and considered in more detail by Fano and J. W. Cooper (cited by Rau and Fano). In addition another effect (« electron leakage ») has to be anticipated when the barrier summit exceeds the ionization limit, a condition that is met for $f$-electrons over a significant range of Z-values. An electron of positive energy can be trapped inside the potential barrier, as an alpha particle of positive energy is trapped inside the nuclear potential. As the leakage of the alpha particle out through the barrier manifests itself in alpha radioactivity, so the quantum mechanical tunneling of the atomic barrier will lead to « electron leakage ». For more than one excited state of a nucleus one sees evidence of the competition between two modes of decay: alpha emission vs. emission of a gamma ray. In the kind of excited state of an atom under discussion here there will be a similar competition between electron leakage and photon emission (electron dropping from $f$-state to an unoccupied $d$-state). In consequence the spectral line will have a breadth $\Gamma = \Gamma_{\mathrm{rad}} + \Gamma_{\mathrm{leak}}$ over and above what would be expected from the rate of radiation alone. It is not clear that this effect has ever been observed in an atom. It is to be distinguished from two well known effects, predissociation in a molecule

(more in the report of Robert Powers ([50])) to tie the particularities and periodicities of chemistry to the continuity of dynamics!

## Six Lessons from the History of the Atom for Gravitational Collapse.

In the history of «atomic collapse» and its epilogue of «true chemical mechanics» six lessons stand out of relevance to the crisis of gravitational collapse («much into little»). First, much emerges from little. The physics of solids, gases, liquids and light, as well as chemistry with all its richness, spring out of something so simple as the quantum mecha-

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(atoms «leaking apart» by penetration through molecular potential barrier) and autoionization or Auger effect in an atom (one electron dropping to a tightly bound state, giving enough energy to another electron to eject it from the atom) a two-electron process in contrast to the one-electron process of «electron leakage». For some of the literature on autoionization see the original paper of Russell and Saunders on Russell-Saunders coupling, where they speak of evidence for states beyond the ionization limit; the work of A. G. Shenstone on the spectrum of copper; the section on autoionization on pp. 7-51 and 7-52 in the chapter of J. R. McNally, Jr. in E. U. Condon and H. Odishaw, eds., *Handbook of Physics*, McGraw-Hill, New York, 2nd ed., 1967 and comments on barrier penetration in the 1935 book of Condon and Shortley cited there; the *Introductory Remarks* of U. Fano in *Radiation Research* 1966, North-Holland, Amsterdam 1967; and the recent review article by U. Fano, *Doubly Excited States of Atoms* in «Atomic Physics», Plenum Press, 1969). It would seem possible to make approximate estimates of the mean life $\tau_{\text{leak}} = h/\Gamma_{\text{leak}}$ with respect to this process by straightforward application of the Gamow theory of decay,

$$I = (1/\hbar) \int_{\text{barrier}} (2m)^{1/2}(V_{\text{eff}} - E)^{1/2} dr$$

with the Hill-Wheeler correction,

$$\tau_{\text{leak}}^{-1} = \Gamma_{\text{leak}}/\hbar = \nu_{\text{class}}/(e^{2I} + 1)$$

making use of the atomic potentials listed by F. Herman and S. Skillman (*Atomic Structure Calculations*, Prentice-Hall, Englewood Cliffs, New Jersey 1963) as employed by S. T. Manson and J. W. Cooper, «Phys. Rev.» **165**, **126** (1968), by A. R. P. Rau and U. Fano, «Phys. Rev.» **167**, 7 (1968), and by S. T. Manson, «Phys. Rev.» **182**, 97 (1969). Compared to this leakage rate it is difficult to name any quantity characteristic of an atom which will vary periodically through the atomic table over a greater range of order of magnitude. The very smallness of some of the expected line widths seem to pose difficulties for the observation of the resonances expected in (*a*) the inverse process of electron scattering, and to make more appropriate as means to detect and observe «electron leakage» in its «direct outgoing form»: (*b*) measurements of line broadening and (*c*) direct measurements of lifetimes of the «leakage states».

([50]) R. Powers, *Frequencies of Radial Oscillation and Revolution as Affected by Features of a Central Potential*, these «Mendeleev Proceedings», 1971.

nics of a system of point charges. Second, such astonishing features of nature as chemical valence and bond directivity give little hint of the simplicity of the underlying machinery. Third, « interactions » as different in strength as ionic forces, homopolar forces, and Van der Waals forces all take their origin in elementary electrostatics. Fourth, to bring to light even the gross anatomy of an atom took probing at the scale of the nucleus (alpha particle scattering). Fifth, most of the dynamics of nature is frozen out. Only so does the individuality of the lowest quantum state so often manage to assert itself. This apparent annihilation of degrees of freedom, seen in a nucleus, in Dirac's sea of negative energy states, in an atom, a molecule, or a crystal lattice, is nowhere more clearly illustrated than in the famous formula for the freezing out of freedom for an oscillator:

$$E = \hbar\omega/(e^{\hbar\omega/kT} - 1) \begin{cases} \nearrow kT & \text{for high } T \text{ (unfrozen)} \\ \searrow \hbar\omega e^{-\hbar\omega/kT} & \text{for low } T \text{ (frozen!)} \end{cases}$$

(Einstein ([51]), 1907). Sixth, like Merlin the magician, the quantum principle kept changing its shape as it was pursued.

To Mendeleev the Merlin principle was « individuality limited by the universal ». To Planck the principle appeared as the element of discreteness in oscillator energies. To Rutherford and Soddy the everchanging mystery showed itself in a strictly probabilistic law for radioactive transformations. To Bohr the mutating magic first manifested itself as a principle for the quantization of angular momentum. Then to Bohr and Einstein it showed itself in the guise of transition probabilities. To Sommerfeld it became a prescription for the quantization of action variables. To Heisenberg the quantum principle showed in the non-commutative algebra of physical quantities, and then in the uncertainty principle. To de Broglie and Schroedinger it manifested itself in the laws of standing and running waves. Pursued further by Bohr, Merlin's mystery grew in stature, becoming in turn the « principle of complementarity » and the « principle of wholeness ». To Feynman it became the principle of « sum of probability amplitudes over all histories », with a democratically equal weight for every history. Today all these forms are recognized as belonging as separate attributes to one logically self-consistent but still not fully apprehended grandeur. The greatness of an advance in physics may be measured by the enlargement it makes in our vision of the quantum principle.

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([51]) A. Einstein, *Die Plancksche Theorie der Strahlung und die Théorie der spezifischen Wärme*, « Ann. der Physik » **22**, 180-190 (1907).

## Much Out of Little.

No firing line where a new advance may be sought calls more clearly today than the crisis of gravitational collapse, nor holds out greater challenges, nor promises more lessons (1) Much out of little? The collapse of a star is of a kind with, and a «laboratory» model for, the collapse envisaged by Einstein for the universe itself [52]. It is therefore also a model, at the other end of time, for the original burst that brought into being the present universe and everything within it, «processed» through fantastically small dimensions and fantastically high densities. The stakes in the analysis are hard to match: the dynamics of the largest object, space, and the smallest object, an elementary particle — and how both began.

*A*. There is no «spontaneous generation».

*B*. But life began!

*A*. There is no «creation or destruction of baryons».

*B*. But baryons began!

## Astonishing Features from Simple Machinery.

(2) Astonishing features from simple machinery? The central doctrine is Einstein's standard battle-tested 1915 geometrodynamics [53]. It is the first description of nature to make geometry a part of physics. No purported discrepancy with its predictions has ever stood the test of time. No logical inconsistency in its foundations has ever been detected. No

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[52] Einstein counted relativity theory as consisting not only of the field equations, but also of something in the nature of a boundary condition, based upon Mach's principle, requiring that the universe be closed, and leading to the consequence that the universe expands, reaches a maximum dimension, and recontracts. In this connection see the remarks of Einstein at the end of the chapter on Mach's principle in his book, *The Meaning of Relativity*, Princeton University Press, Princeton, New Jersey, 3rd ed., 1950, p. 107. For more on Mach's principle envisaged as a boundary condition for the solution of Einstein's field equations, see the relevant parts in the chapters by J. A. Wheeler, and the references cited there, in the books *Relativity, Groups and Topology*, ed. by C. and B. DeWitt, Gordon and Breach, New York 1964 and *Gravitation and Relativity*, ed. by H.-Y. Chiu and W. F. Hoffmann, W. A. Benjamin, New York 1964.

[53] For an account of Einstein's theory oriented towards modern physical applications see for example C. W. Misner, K. S. Thorne and J. A. Wheeler, *Gravitation*, Freeman, San Francisco, scheduled for publication fall 1972.

acceptable alternative has ever been put forward of comparable simplicity and scope. It predicted something so preposterous as the expansion of the universe (54) before that expansion had been observed (55). It predicted that the time linearly extrapolated back to the start of the expansion («Hubble time», $t_H = H^{-1}$) should be greater than $1.5t_0$, where $t_0$ is the actual time back to the start of the expansion (effect of slowing down of expansion) at a date when the measurements indicated $t_H < 0.3t_0$ (era of theories of «continuous creation of matter» and «steady state universe») and years before the more than five-fold error in the Hubble scale of distances had been discovered. In general relativity the equation for the motion of a particle in a known field has been shown not to be needed as a special postulate, as in every other formulation of physics; it follows as a consequence of Einstein's geometrodynamic field equations themselves. Einstein's theory counts the topology as well as the geometry of space as information to be derived out of nature itself, not as decrees of Euclid. The existence of electric charge no longer requires one to assume that Maxwell's equations fail at certain points, or to accept the hypothesis that there exists in nature a magic electric jelly beyond further explanation. Electricity admits of interpretation as lines of force trapped in the topology of a multiply connected space (56).

Whether matter also can be understood as a manifestation of curved empty space, as proposed by W. K. Clifford of the Clifford algebras at the Cambridge Philosophical Society 21 February 1870, is one of the greatest of unanswered questions. It is of no help in answering this question to know that a geon (57) in principle can be constructed out of a collection of electromagnetic radiation or gravitational radiation. Such an object, to admit of classical analysis, must be more massive than the sun!

At small distances the natural object of attention is not the deterministic evaluation of the geometry of space with time as predicted by

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(54) A. FRIEDMANN, *Ueber die Krümmung des Raumes*, «Zeits. f. Physik» **10**, 377 (1922).

(55) E. P. HUBBLE, *A Relation between Distance and Radial Velocity among Extra-galactic Nebulae*, «Proc. Nat. Acad. Sci.» **15**, 168-173 (1929).

(56) J. A. WHEELER, *Superspace and the Nature of Quantum Geometrodynamics*, a chapter in C. DEWITT and J. A. WHEELER, eds., *Battelle Rencontres: 1967 Lectures in Mathematics and Physics*, Benjamin, New York 1968. This chapter, augmented, appears in German as the book *Einsteins Vision*, Springer, Berlin 1968. For literature on the topological interpretation of electric charge see reference 36 in either the chapter or the book.

(57) Geons: J. A. WHEELER, *Geometrodynamics*, Academic Press, New York 1962.

Einstein's equations, but the quantum fluctuations, $\delta g_{\mu\nu}$, in this geometry in a region of observation of extension $L$,

$$\delta g \sim L^*/L,$$

where

$$L^* = (\hbar G/c^3)^{1/2} = 1.6 \times 10^{-33} \text{ cm}$$

is the Planck length. These fluctuations occur everywhere throughout all space. At distances of the order of the Planck length they are so large ($\delta g \sim 1$) that no natural escape is evident from concluding that fluctuations occur as well in the topology of space as in its geometry. On this view those geometries of space which occur with appreciable probability amplitude are characterized everywhere by the most varied submicroscopic structure and varied topology (« foamlike structure of space in the small »). For the effective energy density of these fluctuations order-of-magnitude estimates give

$$\varrho = (\text{energy density}/c^2) \sim \hbar c/L^{*4}c^2$$
$$= c^5/\hbar G^2 \sim 10^{95}\ g/\text{cm}^3 .$$

A bit of nuclear matter with its density of $\sim 10^{14} g/\text{cm}^3$ is completely unimportant by comparison. A particle means less to the physics of the vacuum than a cloud ($10^{-6} g/\text{cm}^3$) means to the physics of the sky ($10^{-3} g/\text{cm}^3$). No single fact points more powerfully than this to the conclusion that a «particle» is not the right starting point for the description of nature.

If a particle is of geometrodynamical origin, it is not a « wormhole » in the geometry of space ($\sim 10^{-33}$cm), for its extension is enormous by comparison ($\sim 10^{-13}$cm). Moreover its energy ($\sim 10^{-27} g$ to $10^{-24} g$) is negligible by comparison with the energy associated with a single «wormhole » (the Planck massenergy, $(\hbar c^3/G)^{1/2} = 2.2 \times 10^{-5} g$). Neither can it be a classically describable deformation in the geometry of space (energy density negligible compared to the effective energy density of the quantum fluctuations!) No possibility has ever presented itself for a quantum geometrodynamic interpretation of a particle but this: the particle is not any individual $10^{-33}$ cm fluctuation in the geometry of space; instead, it is a fantastically weak alteration in the pattern of these fluctuations, extending over a region containing very many such $10^{-33}$ cm regions. In brief, a particle is a quantum state of excitation of the geometry; it is a *geometrodynamical exciton* ([56]). If this updating of the vision of Clifford and Einstein makes sense, then one can summarize its content in one sentence: The physics of particles is the chemistry of the continuum.

### Interactions of Varied Strength from a Single Origin.

3) Interactions of the most varied strength derive from a single elementary origin? Bring together two regions, each of extension $10^{20}$ times as great as the size of a single wormhole, and let the pattern of fluctuation be modified in each as would be suggested by the concept of « exciton ». Then in the region of overlap the pattern will be modified still further. However small the resulting fractional alteration in effective energy density of fluctuations may be in the region of overlap, that basic density itself is so enormous ($\sim 10^{95} g/cm^3$) that the resulting net energy of interaction can as well have one magnitude as another. Thus the possibility would not seem to be excluded to conceive of strong forces, weak forces, and intermediate forces as no more distinct in their character than Van der Waals forces, ionic forces, and valence forces. On this interpretation elementary particle interactions are not primordials; they are residuals.

### Work Up from Small Distances.

4) Work up from small distances rather than work down from large distances? If one had first to know of the existence of the nucleus before he could make progress on the constitution of the atom, it would not seem unnatural to recognize the fluctuation in the geometry of space at the Planck scale of distances as the first step in understanding the constitution of a particle. However, between the one layer of structure at $10^{-33}$cm and the other at $10^{-13}$cm it is not clear in advance how many intermediate layers of structure interpose themselves to complicate the situation. It is conceivable that the situation is much simpler than one might fear. In any case three remarks are in order about the significance of the Planck length. First, it measures the unavoidable indeterminism imposed by the uncertainty principle on the geometry of space (known precisely at one instant, it cannot be predicted precisely at the next!) In effect the phenomenon of gravitational collapse is going on all the time at this submicroscopic scale of distances, and all the time is being undone again. Second, as collapse proceeds the effective radius of a star, or of the universe itself, drops faster and faster, according to classical geometrodynamics. However, it is difficult to imagine that any such deterministic dynamics continues when the dimensions fall below the Planck value. What sets in is more reasonably believed to be much the

same aimless doing and undoing of collapse that characterizes the fluctuation regime, followed eventually (in the case of the universe) by a reexpansion stripped of all memory of the phase of contraction. Third, any truly quantitative treatment of either the fluctuations or the probabilistic coupling between collapse and reexpansion would seem to be excluded until the analysis can take into account fluctuations as well in topology as in geometry. Physics burst out of the straightjacket of Euclidean geometry in coming to an understanding of gravitation. That it must also unlock itself from the fixed connectivity postulated by classical differential geometry would seem an inescapable consequence of the quantum principle. If in coming to terms with « indeterminism » one also finds it unavoidable to abandon the concept of the dimensionality of space at the smallest distance, and retreat to the position that « three » has a meaning only on the average, that development will come as no surprise (« pregeometry ») ([58]). Thus, when a handle in the topology breaks, the handle becomes thinner and thinner until at last only a single point remains to connect two fingers of space. Then even that contact ends. Two points that were neighbors have parted company. However, no such transition can be discontinuous, according to quantum theory. The two points must retain some residual connection after they have separated. If these two points have a residual connection, then every two points must have some connection, one with another — a view of the structure of space very different from that supplied by classical differential geometry!

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([58]) For tentative attempts to assess the nature of « pregeometry », see J. A. WHEELER, p. 335 and pp. 495-500 in the chapter, *Geometrodynamics and the Issue of the Final State* in C. DEWITT and B. DEWITT, eds., *Relativity, Groups and Topology*, Gordon and Breach, New York 1964; p. 40 in the chapter, *Particles and Geometry*, in CARMELI, FICKLER and WITTEN, *Relativity* (1969 Cincinnati conference), Plenum Press, New York 1970; and report, *Pregeometry*, presented at Gwatt, Bern, 15 May 1970 (unpublished). The author is indebted to Robert Geroch for pointing out that topology as studied in many modern contexts does not deal with points individually, but with collections or sets, *called* collections of points, even though one never narrows down the focus to the sharpness where one deals with any individual point as such. This noted, he points out, one recognized that certain relations that might otherwise seem obvious really require proving along such lines as those spelled out for example by J. W. KELLEY, *General Topology*, Van Nostrand, Princeton, New Jersey 1955. In connection with this thought that the concept of set lies deeper than the concept of point, Valentine Bargmann kindly stresses the interest that attaches to Alexander lattices (J. W. ALEXANDER, *The combinatorial theory of complexes*, « Ann. of Math. » **31**, 294 (1930) and later publications).

## The Freezing Out of Dynamics.

5) Most of the dynamics «frozen out»? What goes on at the scale of the Planck distance, and distances larger by many orders of magnitude, has associated with it characteristic quantum energies of the order of $10^{28}$eV and many powers smaller but, even so, far too high to be unfrozen by any devices at the command of physics today. The vacuum is going to go on looking as innocent of structure to the explorer of the atom and the nucleus as a sheet of glass emerging from the rolling mill looks innocent of structure to the operator!

## Enlarging the Vision of the Quantum Principle.

6) An enlargement of our vision of the quantum principle? None has come out of general relativity — yet! History has gone rather the other way around. The quantum principle has been more effective than any single force in the last two decades in driving one into a deeper understanding of the content of Einstein's standard geometrodynamics — even at the classical level. That understanding, won through the labors of many investigators (59),

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(59) Quantization of general relativity in a context not specially emphasizing that it deals with the dynamics of *three*-dimensional geometry: L. Rosenfeld, «Annalen der Physik **5**, 113 (1930) and «Z. Physik» **65**, 589 (1930) and «Annales de l'Institut Henri Poincaré» **2**, 25 (1932); P. G. Bergmann, «Phys. Rev.» **75**, 680 (1949); P. G. Bergmann and J. H. M. Brunings, «Rev. Mod. Phys.» **21**, 480 (1949); Bergmann, Penfield, Schiller, and Zatzkis, «Phys. Rev.» **78**, 329 (1950); P. A. M. Dirac, «Can. J. Math.» **2**, 129 (1950); F. A. E. Pirani and A. Schild, «Phys. Rev.» **79**, 986 (1950); P. Bergmann, «Helv. Phys. Acta», Suppl. IV, 79 (1956), «Nuovo Cimento» **3**, 1177 (1956) and «Rev. Mod. Phys.» **29**, 352 (1957); C. W. Misner, «Rev. Mod. Phys.» **29**, 497 (1957); B. S. DeWitt, «Rev. Mod. Phys.» **29**, 377 (1957); P. A M Dirac, «Proc. Roy. Soc. (London)» A**246**, 326 and 333 (1958) and «Phys. Rev.» **114**, (1959) 924; B. S. DeWitt, *The Quantization of Geometry*, a chapter in «Gravitation: An Introduction to Current Research» (L. Witten, ed.), Wiley, New York, 1962; J. Schwinger, «Phys. Rev.» **130**, 1253 (1963) and **132**, (1317) (1963); R. P. Feynman, mimeographed letter to V F. Weisskopf dated 4 January to 11 February 1961; «Acta Physica Polonica» **24**, 697 (1963); «Lectures on Gravitation» (notes mimeographed by F. B. Morinigo and W. G. Wagner, California Institute of Technology, 1963); report in «Proceedings of the 1962 Warsaw Conference on the Theory of Gravitation» (PWN-Editions Scientifiques de Pologne, Warszawa 1964); S. N. Gupta, report in «Recent Developments in General Relativity», Pergamon, New York 1962; S. Mandelstam, «Proc. Roy. Soc. (London)» A**270**, 346 (1962) and «Annals of Physics» **19**, 25 (1962); J. L. Anderson in «Proceedings of the 1962 Eastern Theoretical Conference» (M. E. Rose, ed.), Gordon and Breach, New York 1963, p. 387; I. B. Khriplovich, *Gravitation*

is summarized by no phrase so well as the single word « superspace » ([60]).

Superspace is the arena in which the dynamics of space unfolds. One point in superspace represents one « geometry » or one special distribution of curvature over a closed 3-dimensional manifold. Another point in superspace represents another such « 3-geometry ». Fig. 3 illustrates a simplified version of superspace. It is endowed with 98 dimensions, whereas superspace proper has infinite dimensionality. A single point in this 98-dimensional space, via its projections on the 98 coordinate axes, determines in one stroke 98 « edge lengths », $L_1$, $L_2$, ..., $L_{98}$. Ninety eight « bones » with precisely these lengths build up (Regge ([61])) a skeleton 3-geo-

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*and Finite Renormalization in Quantum Electrodynamics* (mimeographed report, Siberian Section Academy of Science, U.S.S.R., Novosibirsk 1965); H. Leutwyler, « Phys. Rev. » **134**, B1155 (1964); B. S. DeWitt, *Dynamical Theory of Groups and Fields*, in « Relativity Groups and Topology » (C. DeWitt and B. DeWitt, eds.), Gordon and Breach, New York, 1964; S. Weinberg, « Phys. Rev. » **135**, B1049 (1964), **138**, B988 (1965), and **140**, B516 (1965); M. A. Markov, « Progr. Theor. Phys., Yukawa Suppl. », 1965, p. 85.

Quantization recognizing the *three*-dimensional character of the dynamic entity: P. W. Higgs, « Phys. Rev. Letters » **1**, 373 (1958) and **3**, 66 (1959); R. Arnowitt, S. Deser, and C. W. Misner, a series of papers summarized in *The Dynamics of General Relativity*, in « Gravitation: An Introduction to Current Research » (L. Witten, ed.), Wiley, New York 1962; A. Peres, « Nuovo Cimento » **26**, 53 (1962); R. F. Baierlein, D. H. Sharp, and J. A. Wheeler, « Phys. Rev. » **126**, 1864 (1962); cf. also the Princeton A. B. Senior Thesis of D. H. Sharp, May 1960 (unpublished); J. A. Wheeler, « Geometrodynamics », Academic Press, New York, 1962, and *Geometrodynamics and the Issue of the Final State*, a chapter in « Relativity, Groups and Topology » (C. DeWitt and B. DeWitt, eds.), Gordon and Breach, New York 1964; B. DeWitt, « Phys. Rev. » **160**, 1113 (1967), **162**, 1195 (1967) and **162**, 1239 (1967); J. A. Wheeler, *Superspace and the Nature of Quantum Geometrodynamics*, a chapter in C. DeWitt and J. A. Wheeler, eds., *Battelle Rencontres: 1967 Lectures in Mathematics and Physics*, W. A. Benjamin, New York 1968 (appears in expanded form, in German, as J. A. Wheeler, *Einsteins Vision*, Springer, Berlin 1968); and chapters by J. R. Klauder, A. Komar, J. A. Wheeler, C. W. Misner and B. DeWitt, and especially the chapter by A. Fischer, *The Theory of Superspace*, in M. Carmeli, S. I. Fickler and L. Witten, *Relativity*, Plenum Press, New York 1970.

([60]) « Superspace »: phrase inspired not least by listening to V. Bargmann, B. DeWitt and C. W. Misner expound at various times the content of the Arnowitt-Deser-Misner canonical formulation of general relativity; first mention found in print, pp. 453, 459, 463, and 495 of *Geometrodynamics and the Issue of the Final State*, cited in reference 59.

([61]) For a complete formulation of classical geometrodynamics in the language of a skeleton 4-geometry, see T. Regge, « Nuovo Cimento » **17**, 558 (1961). For more on this Regge calculus, see pp. 463-494 in *Geometrodynamics and the Issue of the Final State*, cited in ref. 58; and for an actual application on a computer, see C.-Y. Wong, *Application of Regge Calculus to the Schwarzschild and Reissner-Nordstrom Geometries at the Moment of Time Symmetry*, accepted fall 1970 for publication in « J. Math. Phys. ». For the earlier background of « skeletonization »

metry (simplified to a 2-geometry in Fig. 3 for ease of visualization). Make a small displacement of the representative point in the abbre-

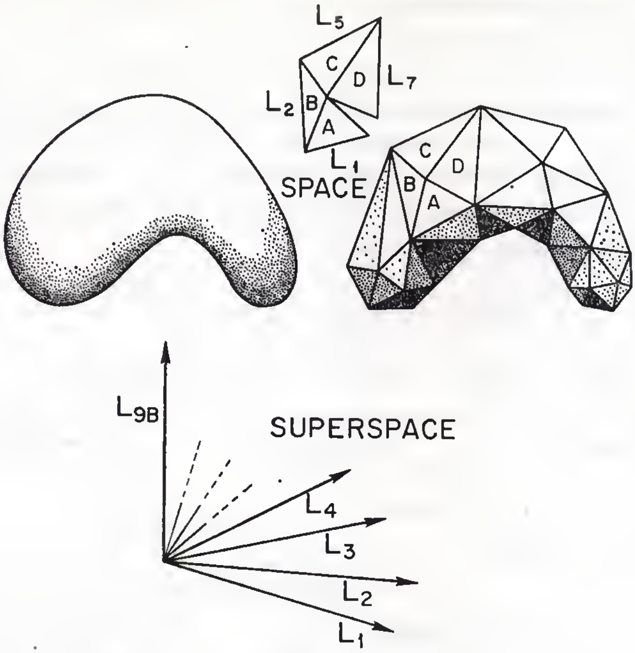


Fig. 3.

Simplified version of superspace. Upper left: a 2-geometry (a stand-in for the 3-geometry of the Einstein universe). Upper right: approximation of this 2-geometry by decomposition into triangles (these 2-simplexes replaced by 3-simplexes (tetrahedrons) in the actual analysis!). The curvature at any vertex (cf. insert) is governed by the nearest neighbor lengths, and by nothing more. The geometry in the simplicial approximation is completely fixed by the specification of the 98 edge lengths. Equivalently (lower diagram) the geometry is completely specified by a single point in a space of 98 dimensions. To go to superspace proper (replacement of simplicial decomposition by actual geometry) one has to go from 98 dimensional space to $\infty$-dimensional space.

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as relevant in topology and differential geometry, see especially S. LEFSCHETZ, *Algebraic Topology*, « Amer. Math. Soc. », New York 1942. In quantum geometrodynamics, where one recognizes that the dynamic object is 3-geometry, the skeletonized manifold differs from that considered by Regge only in this, that it has three dimensions, rather than four. In either three or four dimensions one has options as to the density of skeletonization — denser here, thinner there — for a specified number of bones. Thus some of the displacements in the 98-dimensional version of superspace illustrated in Fig. 3 represent, not true deformations, but mere readjustments as between one place and another in the density of coverage. By adopting a prescription as to how density of vertices will be adjusted to magnitude of curvature, one will wring out these surplus degrees of freedom from the analysis and end up with an abbreviated superspace with a much reduced number of dimensions. In Regge calculus, which is entirely free of coordinates, the variety of ways to reskeletonize one and the same geometry bears some similarities to the freedom that one has as to choice of coordinates in the Ricci calculus of conventional differential geometry.

viated 98-dimensional superspace. Then the 98 edge lengths all change by a small amount. The skeleton 3-geometry undergoes a small deformation. No better illustration can one easily supply as to what it means to speak of the « dynamics of *space* »!

In all the difficult investigations that led at length to the understanding of the dynamics of geometry, both classical and quantum, the most difficult point was also the simplest: The dynamic object is not spacetime. It is space. The geometrical configuration of space changes with time. But it is space, three-dimensional space, that does the changing (compare with particle dynamics, Table III).

TABLE III.

*Geometrodynamics compared with particle dynamics.*

| Concept | Particle dynamics | Geometrodynamics |
|---|---|---|
| Dynamical entity | Particle | Space |
| Descriptors of momentary configuration | $x$, $t$ (« event ») | $({}^3)\ \mathcal{G}$ (« 3-geometry ») |
| History | $x = x(t)$ | $({}^4)\ \mathcal{G}$ (« 4-geometry ») |
| History is a stockpile of configurations? | Yes. Every point on world line gives a momentary configuration of particle | Yes. Every spacelike slice through $({}^4)\ \mathcal{G}$ gives a momentary configuration of space |
| Dynamic arena | Spacetime (totality of all points $x$, $t$) | Superspace (totality of all $({}^3)\ \mathcal{G}$ 's) |

Space, the dynamic entity, and « 3-geometry » or « metric », the precise measure for the momentary configuration of space (« distribution of curvature over space »), have sharply defined meanings as well in quantum geometrodynamics as in classical geometrodynamics. However, given the precise 3-geometry at one instant, one cannot predict ahead to the precise configuration of space at the next instant in quantum theory. The principle of indeterminism forbids. Therefore the concept of spacetime is deprived of any well defined meaning in quantum physics. In contrast, « spacetime » does have a sharp content in classical physics. It records the deterministic classical history of space changing with time. Only in a classical approximation does it make sense to say that there exists any such object as « spacetime », standing like a rigid framework or a marble table, ready to record every event, past, present and future,

with the Einstein interval from each event to its neighbor eternally established.

Go from classical spacetime as one way of specifying a classical history, to a « leaf cutting through superspace » (Fig. 4) as another way of specifying the same classical history. Then turn attention to the quantum description and see why one cannot return from superspace to spacetime!

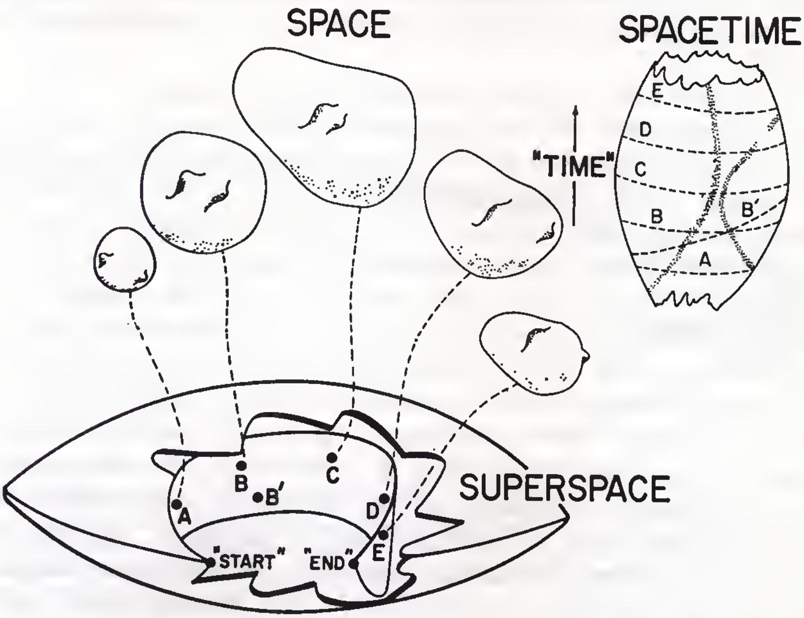


Fig. 4.

Space, spacetime and superspace. Upper left: Five sample configurations attained by space in the course of its expansion and recontraction. Upper right: Spacetime. A spacelike cut, like $A$, through spacetime, gives a momentary configuration of space. (Upper left: the early 3-geometry $A$). Below: Superspace. The one bent « leaf » in superspace (running from « START » to « END ») comprises all those 3-geometries which are obtainable as spacelike slices through the given spacetime.

In the spacetime depicted schematically at the right in Fig. 4, each spacelike slice, such as $A$, through the 4-geometry represents an entire 3-geometry, a momentary configuration for space, a single point in superspace (lower part of Fig. 4). The given spacetime, the given « deterministic classical history of space evolving with time », admits many such slices, $A$, $B$, $B'$, ... etc. For clarity one may speak of these as « YES 3-geometries ». This term distinguishes them from the enormously more numerous « NO 3-geometries » which can never be obtained, try as one will, by making spacelike slices through the *given* 4-geometry, the *given* classical history. The YES 3-geometries, depicted as points in superspace, do not fall on a single line.

No single « time » parameter has the power to order the YES 3-geometries into a one-parameter family. The reason is simple. « Time » in general relativity is not a one-parameter concept. It is a « many-fingered time ». From a given spacelike slice one can move attention forward a little ways into spacetime in an infinitude of ways — « pushing the hypersurface ahead in time » at one rate here, at another rate there. Therefore the given classical history of space, the given spacetime, the given 4-geometry, is mapped, not into a line, but into a leaf cutting through superspace ([62]).

Given the leaf of history cutting through superspace, one can go back and reconstruct the original classical spacetime in three steps: first, from leaf to the points on the leaf; second, from each of these representative points to the corresponding 3-geometry; finally, assemble these 3-geometries into the 4-geometry, as a child assembles and internests a multitude of boxes into a rigidified construction.

Quantum physics does away with the sharp distinction between « YES 3-geometries » and « NO 3-geometries ». It speaks of a probability amplitude $\psi = \psi({}^{(3)}\mathcal{G})$ for this, that and the other 3-geometry. It contrasts strikingly with classical geometrodynamics, with its sharp confinement to a single leaf in superspace. Quantum geometrodynamics gives an equation (last three books cited in reference 59) for the propagation of the probability amplitude $\psi({}^{(3)}\mathcal{G})$ throughout superspace. Almost every 3-geometry has a non-zero probability amplitude. The ${}^{(3)}\mathcal{G}$ 's that occur with significant probability amplitude do not fit and cannot be fitted into any spacetime, any 4-geometry, any classical history of space evolving dynamically with many-fingered time. That ${}^{(4)}\mathcal{G}$, that « magic structure » of classical physics, simply does not exist. Without that building plan to organize the $\mathcal{G}^{(3)}$ 's of significance into a definite relationship, one to another, even such a familiar notion as the « time ordering of events » is devoid of all immediate significance. Only under circumstances where one can neglect the quantummechanical spread of the probability wave-packet in superspace can one treat the dynamical evolution of geometry in the deterministic context of classical general relativity.

These considerations reveal that the concepts of spacetime and time itself are not primary but secondary ideas in the structure of physical

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([62]) There is an infinitude of ways to make a small deformation in a 3-geometry and yet leave its representative point on the leaf. There is a higher order of infinity for the number of ways to deform the 3-geometry so that its representative point moves off the leaf into the surrounding NO-portion of superspace (infinite dimensional « leaf of history » imbedded in a superspace with an overridingly infinite dimensionality).

theory. These concepts are valid in the classical approximation. However, they have neither meaning nor application under circumstances when quantum geometrodynamical effects become important. Then one has to forgo that view of nature in which every event, past, present, or future, occupies its preordained position in a grand catalog called « spacetime ». There is no spacetime, there is no time, there is no before, there is no after. The question what happens « next » is without meaning.

Fig. 5.

Collapse depicted symbolically as coupling one cycle of expansion and recontraction of the universe (heavy « line » in superspace) in region of collapse (cross hatched part of superspace) with other cycles of the universe (alternative « histories of the geometry of space » depicted as « lines » emergent from region of collapse). A fuller picture, still in the context of classical geometrodynamics, would show each one dimensional « line » through superspace expanded to a multidimensional « leaf of history » as shown in the lower part of Fig. 4. This deterministic track through superspace is replaced in quantum general relativity by a propagating wave packet (symbolized by wave crests in diagram). Any deterministic classical analysis breaks down in the crosshatched « region of complete collapse » (dimensions of universe of order of the Planck length $(\hbar G/c^3)^{1/2} = 1.6 \times 10^{-33}$ cm). What goes on there is envisaged as analogous (*a*) to the scattering of the de Broglie wave of an electron by the Coulomb field of a point charge or (*b*) to the coupling of waves in separate wave guides at a wave guide junction.

Nowhere do these consequences of the quantum principle have more immediate application than in the phenomenon of gravitational collapse. Nowhere are the differences greater between the classical and the quantum pictures of the dynamics. A computer following the collapse according to the sharply deterministic prescription of classical geometrodynamics comes to the point where it cannot go on (heavy arrow in Fig. 5 leading directly to the singular collapse domain of superspace). This prediction can only be compared with a prediction of classical mechanics. A particle headed directly towards a point center of Coulomb attraction will arrive in a finite time at a condition of infinite kinetic energy according to Newtonian theory. In actuality the particle is described by a wave packet.

It experiences, not deterministic collapse, but probabilistic scattering. No more for the universe than for the particle can one believe that physics comes to an end merely because classical physics comes to the limit of its predictive power! Little one may know about some central details of quantum geometrodynamics, among them especially how to describe quantum mechanical transformations of the connectivity of space. This circumstance in no way impairs one's perception of the broad outline of quantum geometrodynamics and the central lesson of superspace: the universe begins a new cycle of expansion from the same singular region of superspace where collapse lost its way. Moreover, there is not a unique history that leads out of this singular region. There is a probability distribution of histories. Each of these alternative cycles of the universe has a different set of determinants: a different volume at the phase of maximum expansion and a different lapse of time from the start of expansion to the end of recontraction. No escape is evident from this picture of what goes on: The universe transforms, or transmutes, or «transmigrates» probabilistically from one cycle of history to another in the era of collapse.

If to describe this process requires one to burst the bounds of classical differential geometry, this will not be the first time that physics has given the lead to mathematics, nor the quantum principle the lead to physics.

However straightforwardly and inescapably this picture of the transformations of the universe would seem to follow from general relativity and the quantum principle, the two overarching principles of 20th century physics, it is nevertheless fantastic to contemplate. How can the dynamics of a system so incredibly gigantic be switched, and switched at the whim of probability, from one cycle that has lasted $10^{11}$ years to another that will last only $10^6$ years? At first only the circumstance that the system gets squeezed down in the course of this dynamics to incredibly small distances reconciles one to a transformation otherwise so unbelievable. Then one looks at the upended strata of a mountain slope, or a bird not seen before, and marvels that the whole universe is incredible:

mutation of a species
metamorphosis of rock
chemical transformation
spontaneous transmutation of a nucleus
« transmigration » of the universe.

If it cast a new light on geology to know that rocks can be raised and lowered thousands of meters and hundreds of degrees, what does it mean for physics to think of the universe as from time to time « squeezed through a knot-hole », drastically « reprocessed », and started out on a

fresh dynamic cycle? Four considerations press themselves to one's attention. *a*) No known quantity is conserved in the dynamic evolution of a closed model universe endowed with no special symmetry. Thus, there is no platform on which to stand « outside the universe » to measure its mass-energy or angular momentum, via effects on Kepler orbits or otherwise. Therefore it is not surprising that the energy and angular momentum of the universe are not even defined, let alone conserved. Consequently it is difficult to see what determinant could continue unchanged in value from cycle to cycle of the universe, even any determiner of the spectrum and masses of the elementary particles.

## Reprocessing Matter: Molecules, Nuclei, Particles.

*b*) Molecules are reprocessed in a flame to new molecules. Nuclei are reprocessed in a star to new nuclei (63). In the overwhelming rage of gravitational collapse what escape is there from believing that the spectrum of elementary particles is reprocessed (Table IV) to a new spectrum? Must not the particle of today be viewed as fossils from that early turmoil as the molecules and nuclei of today are also viewed as fossils from events of lesser violence? With no determinant left alive from cycle to cycle of the dynamics to perpetuate the spectrum of the particles, no alternative is evident but to conclude that that spectrum must be extinguished and start with a new pattern after each collapse. One is reminded of the fixity of geological strata between one period of metamorphosis and the next!

On this view the present spectrum of particle masses, and even the net numbers of baryons and leptons in the universe today, cannot be regarded as fundamental constants of nature. They are rather to be undestood as in the nature of initial conditions relevant to this cycle of the universe alone. The so-called « big numbers » ($\sim 10^{80}$ particles in the universe; $\sim 10^{40}$ ratio of radius of universe at maximum expansion to effective size of an elementary particle; $\sim 10^{40}$ ratio between elementary particle dimensions and the Planck length) (64) have never received a

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(63) Long before there was any direct evidence for the thermonuclear reactions, it will be recalled, Eddington gave reasons why it was in escapable that nuclear reactions deep in the interior of a star must be responsible for its output of energy, and remarked that if a critic did not believe the temperature there to be high enough, « let him go and find a hotter place ».

(64) A. S. Eddington, *Relativity Theory of Protons and Electrons*, Cambridge Univ. Press, 1936, and *Fundamental Theory*, Cambridge Univ. Press, 1946; also « Proc. Camb. Phil. Soc. » **27**, 15 (1931); P. A. M. Dirac, « Nature » **139**, 323 (1937), « Proc. Roy. Soc. (London) » **A165**, 199 (1938); P. Jordan, *Schwerkraft und Weltall*,

TABLE IV.

*Collapse of universe predicted by classical theory, compared and contrasted with classically predicted collapse of atom.*

| System | Atom | Universe |
|---|---|---|
| Dynamic entity | System of electrons | Geometry of space |
| Nature of classically predicted collapse | Electron headed towards point center of attraction is driven in a finite time to infinite energy | Not only matter but space itself arrives in a finite proper time at a condition of infinite compaction |
| One rejected «way out» | Give up Coulomb law of force | Give up Einstein's field equations |
| Another rejected proposal | « Accelerated charge need not radiate » | « Matter cannot be compressed beyond a certain density by any pressure, however high » |
| How this proposal violates principle of causality | Coulomb field of point charge cannot readjust itself with infinite speed out to indefinitely great distances to sudden changes in velocity of charge | Speed of sound cannot exceed speed of light; pressure cannot exceed density of mass-energy |
| A major new consideration introduced by recognizing quantum principle as over arching organizing principle of physics | Uncertainty principle; binding too close to center of attraction makes zero-point kinetic energy outbalance potential energy; consequent existence of a lowest quantum state; can't radiate because no lower state available to drop to | Uncertainty principle; propagation of representative wave packet in superspace does not lead deterministically to a singular configuration for the geometry of space; leads rather to a probability distribution of outcomes, each outcome describing a universe with a different size, a different set of particle masses, a different number of particles, and a different length of time required for its expansion and recontraction. |

Vieweg und Sohn, Braunschweig, 1955, and « Z. Physik » **157**, 112 (1959); R. H. DICKE, « Science » **129**, 3349 (1959), « Nature » **192**, 440 (1961), and *The Theoretical Significance of Experimental Relativity*, Gordon and Breach, New York 1964, p. 72; and S. HAYAKAWA, « Progr. Theor. Phys. » **33**, 538 (1965) and « Progr. Theor. Phys. Suppl. », p. 532 (1965).

physical explanation. They never will, if they are initial value data! Physics can unravel dynamic law, but it has never found what principle fixes the other half of dynamics, the «initial conditions» of nature.

Physical explanation for the large numbers, no; biological explanation, perhaps. Brandon Carter has given reasons to believe that determinants substantially different from those that characterize the present cycle of the universe would have made the development of life difficult if not impossible (65).

*c*) No debate of old seems more fruitless on rereading than this: can there exist a multiplicity of universes? (66). Warned by the inconclusive nature of the arguments advanced on both sides, how can a thinking man return today to that old quagmire of reason? Today it is not a matter of choice. The superspace of Einstein's standard 1915 geometrodynamics, one now realizes, compels one to ask how one cycle of the dynamics of the universe is coupled to another, and even supplies the beginning of a framework for the answer. Is there no way, however, to tie down such cosmic considerations to something more concrete? Happily there is.

The collapse of the white dwarf core of a star to a black hole provides a kind of «laboratory model» in which one can hope to see and test some of the effects predicted in the collapse of the universe itself. Of these

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(65) That entropy will increase, radiation will be retarded, life will evolve forward, and black holes will absorb after the universe moves from the phase of expansion to the phase of recontraction is guaranted by no experience whatsoever and may even be questioned: L. Boltzmann and N. Wiener, as referred to in *The Nature of Time*, ed. by T. Gold, Cornell University Press, Ithaca, New York, in which see also J. A. Wheeler, pp. 28-29, 46-47, 60-61, 73-74, 78-79, 90-107, 116-117, 142, 186, 233-240; also G. W. Leibniz, *Essais de Théodicée sur la bonté de Dieu, la liberté de l'homme, et l'origine du mal*, Amsterdam 1747; S. Clarke, *A Collection of Papers which passed between the late Learned Mr. Leibniz, and Dr. Clarke, In the Years 1715 and 1716. Relating to the Principles of Natural Philosophy and Religion*, London 1717; L. D. Landau and E. M. Lifshitz, *Statistical Physics*, trans. E. Peierls and R. F. Peierls, Addison-Wesley, Reading, Massachusetts and Pergamon, London 1958; R. H. Dicke, *Dirac's Cosmology and Mach's Principle*, «Nature», November 1961; B. Carter, *Large Numbers in Astrophysics and Cosmology*, preprint, Institute of Theoretical Astronomy, Cambridge, England, September 1968; J. A. Wheeler, *Man's Place in Cosmology*, Léon Lecture, University of Pennsylvania, 11 Nov. 1969 (unpublished); pp. 71-72 in J. A. Wheeler, *The Universe in the Light of General Relativity*, «The Monist» 47, 40 (1962); W. J. Cocke, «Phys. Rev.» **160**, 1165 (1967); F. Zerilli, unpublished calculations, Princeton, 1967, on effect of approach to moment of statistical symmetry on relative rates of radioactive transformations of long and short half lives.

(66) Ruling of Bishop of Paris in 1228 that it is wrong to deny God's power to create as many worlds as He pleases; cf. also writings of William of Ockham and a modern recapitulation by Gordon Leff.

effects none is more striking than the wiping out of every posibility to tell how many baryons and how many leptons went in (Fig. 1). To start with particles, and end with something indistinguishable from pure geometry, will be encouragement to believe that nature can start with pure geometry and end with particles. To start with something that resists collapse and to end with everything crushed will allow one to continue to believe that the universe itself must collapse.

No one can accept the geometrodynamic interpretation of particles if no one can verify predictions about black holes. Happily three ways offer themselves to test for the existence of these objects and to study their properties: pulses of gravitational radiation given out at the time of formation; x-rays given out by gas heated by compression as it converges onto a black hole; and activity associated with black holes in galactic nuclei ([67]).

*d*) The black hole does not model in every respect the dynamics of the universe. It has an outside, a far away asymptotically flat « platform », where the observer, as payment for not being caught up in the collapse himself, also cannot see the final stages of the collapse, much less any reexpansion. Closely associated with this circumstance is the onesidedness in time of the dynamics of the black hole: it absorbs particles and quanta of radiation, but never emits them.

This onesidedness in time is to be read not out of Einstein's field equations, but out of experience ([68]). One does not need equations to know that heat flows from hot to cold, or that radiation diverges outward from an accelerated charge, but does not converge inward from infinity upon it. What is true of faraway infinity must be true also of « captured infinity », if one may be permitted to give that name to the horizon of a black hole. It can receive. It cannot give.

Nowhere in physics can one name a process where friction (« onesidedness in time ») more dominates dynamics than in the fusion of two black holes: fusion takes place, but fission does not. Is some small modicum of this onesidedness in time inherited by particles, that they should violate CP-invariance? ([69]). Is the process of CP-violation a small pre-

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([67]) For a review, see sections on black holes and gravitational radiation in R. Ruffini and J. A. Wheeler, *Relativistic Cosmology and Space Platforms*, a chapter in *The Significance of Space Research for Fundamental Physics*, European Space Research Organization book SP-52, Paris 1971.

([68]) See however reference 65.

([69]) J. H. Christenson, J. W. Cronin, V. L. Fitch and R. Turlay, « Phys. Rev. Letters » 13, 138 (1964); T. T. Wu and C. N. Yang, « Phys. Rev. Letters » 13, 380 (1964).

monitory signal of the deeper world of geometric physics, as Becquerel's radioactivity betrayed the then hidden world of nuclear physics?

Does the universe today contain equal amounts of matter and antimatter? Or does matter everywhere have the same composition which it does in this vicinity? This question, always interesting, also seemed at one time a deep issue of principle. Not so now! Given equal amounts of the two kinds of matter, in principle one can arrange for a black hole to swallow all the antimatter, leaving only matter behind. No amount of inspection of the black hole will ever reveal the secret of what it did with a once symmetric past.

## From Einstein's Geometrodynamics to an Enlarged Vision of the Quantum Principle.

All of these considerations came up in asking, what does the quantum principle have to contribute to geometrodynamics? Turn back now to the original formulation of question 6. What can geometrodynamics do to unveil more of the content of the quantum principle?

## Everett's "Relative State" Formulation of Quantum Mechanics.

*a*) To ask about the «quantum state of a closed universe» is to displace the «observer» from his usual position outside the system under study. He is inside. No one has found a way to deal rationally with this kind of situation except through Everett's «relative state formulation» of quantum mechanics (70). It abandons the postulate that an observation starts the system off in a fresh quantum state. Instead, it envisages the wave function after an «observation» as the sum of terms («branches of history»), each the product of (i) a factor describing the non-observer part of the system in one quantum state, and (ii) a factor describing the observer in a corresponding «relative state». All branches of the history are viewed as «coexisting» in an ethereal sense, and only in an ethereal sense, a sense perhaps best described by William James (71). «Actualities,

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(70) H. EVERETT, III, «Rev. Mod. Phys.» **29**, 454 (1957); J. A. WHEELER, «Rev. Mod. Phys.» **29**, 463 (1957) and *Geometrodynamics*, Academic Press, New York 1962, p. 75; B. S. DEWITT, *The Everett-Wheeler Interpretation of Quantum Mechanics*, a chapter in C. DEWITT and J. A. WHEELER, eds., *Battelle Rencontres - 1967 Lectures in Mathematics and Physics*, W. A. Benjamin, New York 1968; B. DEWITT, *The Many-Universes Interpretation of Quantum Mechanics*, lectures delivered at International School of Physics «Enrico Fermi», Villa Monastero, Varenna, July 1970.

(71) Appreciation is expressed to Paul Van der Water for this quotation from William James.

he wrote, « seem to float in a wider sea of possibilities from out of which they were chosen; and *somewhere*, indeterminism says, such possibilities exist, and form part of the truth ».

How can these considerations be brought to a sharp focus and definitive resolution? For this purpose no issue would seem more timely or more compelling than the quantum mechanics of the universe. Here, in the context of superspace, one finds himself confronted not only with the coupling between alternative histories of the universe, but even with the « coexistence » of these « histories » (72).

## Monads and Fluctuations.

*b*) Of all the developments that Leibniz gave the world, from the calculus in its modern form to the principle of least action, and from the principle of sufficient reason to the concept of the best of all possible worlds, there was none on which he laid greater weight, and none more puzzling to his contemporaries, than the idea of a world made of monads (73), each of which however subsumes inside itself the whole world, as a microcosm (74). A fluctuation in the geometry of space at the Planck length is a small scale version of the expansion and recontraction of the universe itself. Is the similarity between the two levels of dynamics more than superficial? Are the two really one and the same? Is this the message of the conformal invariance that stares out from so much of physics (75),

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(72) For the clarification of these issues of interpretation the prime desideratum would seem to be a fully developed mathematical formulation of quantum geometrodynamics. Already from the history of wave mechanics one learned that the favorable order of developments was physical idea first; mathematics second; and philosophy of measurement third. The same lesson appeared in the work of N. BOHR and L. ROSENFELD on the measureability of the electromagnetic field quantities: « Kgl. Danske Videnskab Selskab, Mat. fys. Medd. » **12**, 8 (1933) and « Phys. Rev. » **78**, 794 (1950). For the development of the mathematics needed for quantum geometrodynamics, three promising clues offer themselves. One is the extensive knowledge one already has of the mathematics of superspace. Another is what one can say on physical grounds about collapse. The third is the requirement of the quantum principle for fluctuations in the geometry and topology of space.

(73) For a brief account of the concept of « monad » see for example the *Encyclopedia Britannica*, article on Leibniz.

(74) Compare with the principle so well known in biology, « Ontology recapitulates phylogeny ».

(75) For conformal invariance in electrodynamics, see for example K. JOHNSON, R. WILLEY and M. BAKER, « Phys. Rev. » **163**, 1699 (1967) and earlier work cited there; and for conformal invariance in geometrodynamics, see for example section 8

as from a friend temporarily voice less whose intelligence one vainly tries to hear? Are particles identical because each carries within itself the same image of the universe in travail giving birth to them all? ([76]). One will have a larger view of the quantum principle when one knows the answers to these questions!

### Much into Little as the Key to Winning Much out of Little.

From Mendeleev's atom to the collapsing star, from the dynamics of a system of particles to superspace and the dynamics of geometry, a central theme stands out: much out of little, richness from simplicity, individuality out of continuity, Pythagoras and Plato reconciled in the principle of Planck; and the emblem of this theme? A continuous potential binding a continuous wave with a discrete number of nodes and a discrete energy value! ([77]).

Much into little is the other theme; *collapse*; the collapse of the atom that was not collapse; the collapse of the star and the universe itself, rated as inescapable by Einstein's battletested theory; the collapse satisfying the guiding principle of Bohr's life work: no progress without a paradox!

The paradox of atomic collapse, attacked with the weapon of the quantum principle, led to « chemical mechanics ». No cheap way offered itself out of that paradox. None offers itself now out of the new paradox, crisis in the theoretical physics of our day. Not long can one believe it will be until the advance of physics and astrophysics brings direct evidence on black holes to contradict or confirm a central prediction and, either way, sharpen the crisis.

Black holes exist, if standard 1915 general relativity and the simplest elements of astrophysics are right. They are formed from time to time. There is no disposable parameter for a black hole except its mass, charge, and angular momentum. In a black hole all memory is erased of the par-

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of the chapter of R. Penrose, *Structure of Space-Time*, in C. DeWitt and J. A. Wheeler, eds., *Battelle Rencontres: 1967 Lectures in Mathematics and Physics*, W. A. Benjamin, New York 1968.

([76]) Cf. also *Particles and Geometry* ref. 58, for the closely related but not identical view that particles are residuals of primordial turbulence and are to be identified with the lower less rapidly decaying end of the spectrum of this turbulence. The difference is the difference between the Leibniz monad principle and the Misner mixmaster mechanism for bringing about similarity between all particles.

([77]) Appreciation is expressed to V. Bargmann for suggesting this epitome of the quantum principle.

ticularities of the particles that went to build it. In effect a collection of $\sim 10^{57}$ particles is ground down into geometry. Einstein's theory says more: that the universe itself with its $\sim 10^{80}$ particles is also ground down.

Collapse at both levels gives incentive to consider afresh the vision of Clifford and Einstein, that every particle is constructed out of geometry; or, in updated language, a particle is a « geometrodynamic exciton ». The atom is preposterous, with its unbelievable wealth of chemistry built on the dynamics of a few electrons. The nucleus is preposterous, with its many-radiant myriad of energy levels built on the motions of a few nucleons. Can the elementary particle be less preposterous? A Sibyl seems to say, « Choose: paradox or nothing »! Nothing offers for building a particle except the dynamics of space itself. Nothing offers for giving discreteness to this dynamics except the quantum, Mendeleev's « individuality amid continuity ».

The arena for the quantum dynamics of geometry is superspace. Superspace is forced on physics by the union of the quantum principle and standard Einstein geometrodynamics. The mathematical framework of superspace, though understood in broad outline today, still requires some augmentation to accomodate the quantum fluctuations in the topology of space that seem so inescapable at the Planck scale of distances.

As viewed in the context of superspace, gravitational collapse appears as a probabilistic process of scattering (Fig. 5). In each such act of « collapse scattering », space is reprocessed. It is transformed. It « transmigrates ».

Each new cycle of the universe, according to these views, begins with a new spectrum of particle masses. To specify the determiners of the new spectrum is to give initial conditions for the dynamics of the new expansion, a prediction beyond the power of physics to make. The probabilistic character of the « collapse scattering » forbids. On this view it is unrealistic to believe that one will ever be able to calculate the masses of the elementary particles from the principles of physics. To ask physics to give these masses would seem a mistaken question. A better question has rather another turn. Among all the cycles of the universe that run through their histories in superspace, long cycles and big universes being less probable than short cycles and little universes, in which do the determinants have values which will permit life as we know it? ([78]). And what is the spectrum of masses that goes with this set of determinants?

Preposterous it surely is to imagine that the dynamics of the universe can have anything to do with the mass of the proton. Nothing could be more preposterous — except to suppose that the mass of the proton

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([78]) In this connection, see especially G. W. LEIBNIZ and B. CARTER, ref. 65.

has nothing to do with the dynamics of the universe! The crisis of gravitational collapse has launched the physics of our time on an incredible journey, a search to understand the «chemistry of geometry», surely a new zig-zag course from paradox to paradox.

If we want a guide on this odyssey of exploration, one who had a serene and happy approach to mystery, an eye for what is central, the energy to work around and around the vital paradox wherever work was possible, and the sense of harmony to recognize simplicity in the midst of complexity, who better can we choose for our patron saint than Dimitri Ivanovitch Mendeleev?

## Acknowledgment.

Appreciation is expressed to the organizers of this conference and to the two host academies for their hospitality; and to colleages, there and elsewhere, for discussions, among them not least to V. Bargmann, Ugo Fano, Robert Geroch, V. I. Gol'danski, Gertrude and Maurice Goldhaber, S. Gorodetsky, Robert Powers, Emilio Segré, and Claudio Teitelboim, and especially to S. A. Goudsmit for emphasizing in a conversation some years ago the then already long known approximate dependence of energy upon the combination $n_r + 2l$.

I am sure I speak for all participants when I thank our hosts for their hospitality during these days in Torino, not only happy but also scientifically most interesting. We go to Rome, well fortified in Torino not only by elements but also by alimente. To Professor Carlo Ferrari, Presidente della Accademia delle Scienze di Torino, and to the other officers of the Academy, we express our deep appreciation. We cannot fail also to thank the great Lagrange, who greets us every morning, listens benevolently during our meetings, and smiles goodbye to us every evening.

Sono certo di ricevere l'approvazione di tutti i partecipanti nel ringraziare gli organizzatori del congresso per la loro ospitalità durante queste giornate torinesi, che sono riuscite particolarmente felici, non solo dal punto di vista scientifico. Partiamo dunque per Roma. ben provvisti non solo di elementi ma anche di alimenti.

Al Prof. Ferrari, Presidente dell'Accademia delle Scienze di Torino, e ai collaboratori noi rivolgiamo sentiti ringraziamenti. A questo punto è doveroso un ringraziamento al sommo Lagrange che ci ponge il suo saluto ogni mattina, ascolta benevolmente le nostre discussioni e sorridendo ci congeda ogni sera.

ROBERT T. POWERS (*)

# Frequencies of Radial Oscillation and Revolution as Affected by Features of a Central Potential (**).

**Abstract.** — *A parameter describing the classical orbit of a bound particle in a central potential is the ratio of the frequencies of radial oscillation and revolution. This ratio is proportional to the angle swept out by the particle between the apogee and perigee of its orbit. The effect of the form of the potential on this ratio of frequencies is studied for attractive central potentials which vary with a power of the distance from the center of force. The results of this study can be applied to quantum systems, such as the atomic elements, to obtain a qualitative picture of the effective potential as sampled by the outer electrons.*

## 1. Energy Levels and the "Classical Orbits".

It is well known from the electronic configuration of the elements that the order of filling of the electron shells, 1s, 2s, 2p, etc., with increasing atomic number, Z, is such that the sum, $n + l = n_r + 2l + 1$, of the principal quantum number, $n$, and the total orbital angular momentum quantum number, $l$, increases or remains constant as successive electron shells are filled [1]. This suggest that the energy associated with an electron shell is, to a crude approximation, an increasing function of $n + l$. The energy levels of a single outer electron in the heavier elements also confirm this notion that the energy is roughly an increasing function of $n + l$. An example of these energy levels is given in Fig. 1. The principal quantum number is related to the radial quantum number, $n_r$ (which corresponds to the number of nodes in the radial part of the electron wave function) by the relation, $n = n_r + l + 1$. The energy is, then, roughly a function of the quantity $k = n_r + 2l + 1$. The classical quan-

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tities corresponding to $n_r + \frac{1}{2}$ and $l + \frac{1}{2}$ in the so-called «improved $\left(l + \frac{1}{2}\right)$ – JWKB approximation» [2] are the radial action $J_r$ and the angular action $J_\theta$ (divided by the quantum of action, $h$). This implies that the energy of an outer electron, considered classically, is roughly

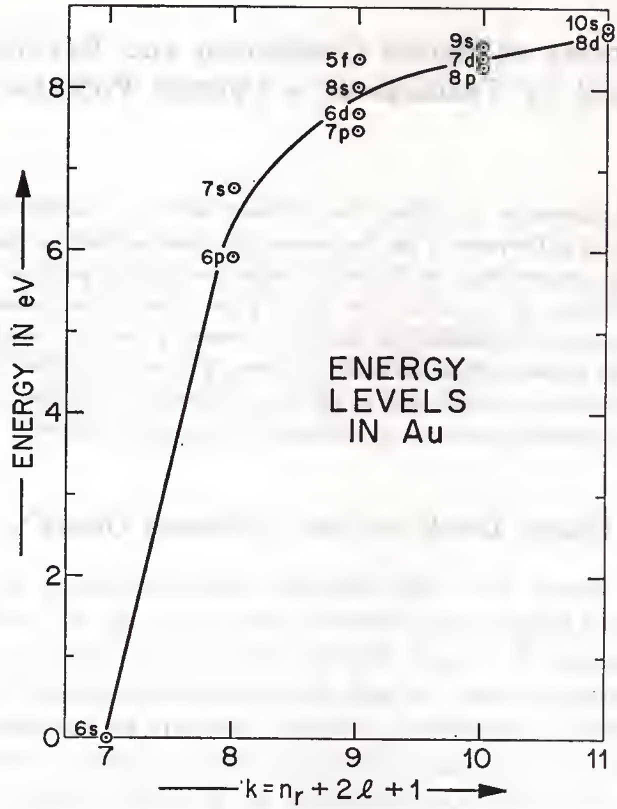


Fig. 1.

The order of energy levels in gold, Au, (in which the 6s electron is excited) as an illustration of the approximate correlation between the energy and the combination of quantum numbers, $k = n + l = n_r + 2l + 1$ (data from tables in Charlotte E. Moore, *Atomic energy levels as derived from the analyses of optical spectra*, National Bureau of Standards Circular 469, U. S. Government Printing Office, Washington, D. C., Vol. 3, 1 May 1958).

a function of the quantity, $J_r + 2J_\theta$, that is, $E = F(J_r + 2J_\theta)$. If $\nu_\theta$ and $\nu_r$ are the angular and radial frequencies of oscillation, it follows from the properties of the action-angle variables [3] that the ratio of these frequencies is,

$$\nu_\theta/\nu_r = (\partial E/\partial J_\theta)/(\partial E/\partial J_r) \approx (\Delta E/\Delta l)/(\Delta E/\Delta n_r) \approx 2\,. \tag{1}$$

Considered classically, the orbit of an outer electron should make approximately two revolutions about the nucleus during the time that it complete one radial oscillation (Fig. 2).

Similary the order of filling of the nuclear levels in the atomic nucleus suggest that the energy is approximately an increasing funtion of the quantity, $2n_r + l$. This implies that the ratio of angular and radial fre-

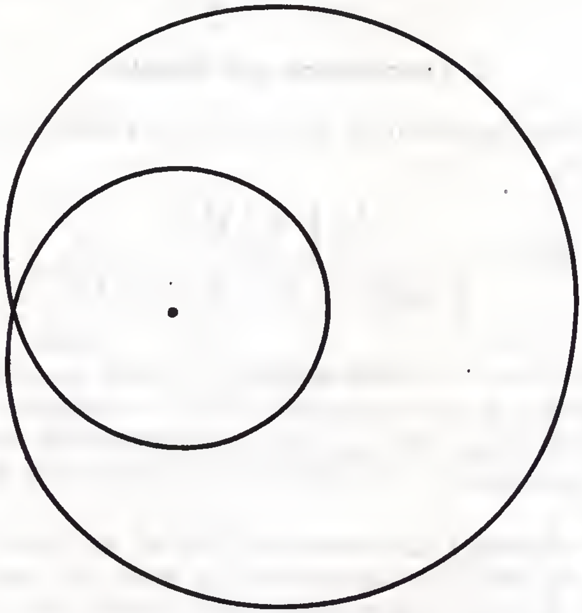

Fig. 2.

An orbit for which the frequency ratio, $\nu_\theta/\nu_r = 2$.
The orbit is shown here for the case where $r_{\text{max}}/r_{\text{min}} = 3$.

quencies is approximately $\frac{1}{2}$. One would then expect the orbit of an outer nucleon to be not unlike the orbit of a particle in an harmonic oscillator potential — the well known model for the effective field in the nucleus [4].

Comparison and contrast between the atom and the nucleus suggest a more general question. What central potential, combined with appropriate initial conditions, will produce a classical orbit such that the ratio, $\nu_\theta/\nu_r$, is some preassigned constant? There are only two potentials for which $\nu_\theta/\nu_r$ is the same for all orbits regardless of the amplitude of the radial oscillation. These are the coulomb potential, for which $\nu_\theta/\nu_r = 1$, and the harmonic oscillator potential, for which $\nu_\theta/\nu_r = \frac{1}{2}$. For

all other potentials this ratio, depends, not only on the potential itself, but on the amplitude of the radial oscillation.

In this paper we give the results for the dependence of the ratio, $\nu_\theta/\nu_r$, on the potential and on orbital parameters for simple attractive potentials, described by power laws:

$$V = (K/s)r^s \qquad (K > 0,\ s \neq 0,\ s > -2).$$

## 2. Calculations and Results.

The differential equation for the orbit of a particle in a central potential, $V(r)$, is

$$dr/d\theta = \frac{\left(l + \frac{1}{2}\right)\Big/ r^2}{\left[(2m/\hbar^2)\,(E - V) - \left(l + \frac{1}{2}\right)^2 \Big/ r^2\right]^{1/2}}. \tag{2}$$

The radial «velocity», $dr/d\theta$, vanishes at apogee, $r_{\max}$, and at perigee, $r_{\min}$. The expression in the denominator of Eq. (2) vanishes at these points. From the values of $r_{\min}$ and $r_{\max}$ one can determine the energy, $E$, and the angular momentum, $l$. The orbit is, then, completely determined by $r_{\min}$ and $r_{\max}$.

It is an advantage to choose potentials of the form, $V = (K/s)r^s$. The shape of the orbit (and consequently the ratio, $\nu_\theta/\nu_r$) does not depend on the size of the orbit, but only the dimensionless ratio, $u = r_{\max}/r_{\min}$. The orbits are invariant with respect to a change of scale. From a knowledge of $u$ and $\nu_\theta/\nu_r$ a qualitative picture of the orbit can be obtained. Sketch a line which starts, perpendicular to the radius vector, at the point, $r = 1$, $\theta = 0$, (in polar coordinates) and spirals outward until it again becomes perpendicular to the radius vector at the point, $r = u$, $\theta = 180^\circ$ $(\nu_\theta/\nu_r)$. The orbit can be extended by symmetry.

The orbits can be characterized by the dimensionless number, $f = J_r/(J_r + J_\theta)$, rather than by the ratio, $u = r_{\max}/r_{\min}$. This new parameter has the advantage that it is directly related (via the correspondence principle) to the quantum numbers $n_r + \frac{1}{2}$ and $l + \frac{1}{2}$; that is, $f \approx \left(n_r + \frac{1}{2}\right)\Big/\left(n_r + \frac{1}{2} + l + \frac{1}{2}\right)$.

In Fig. 3 we give the results for the dependence of the frequency ratio, $\nu_\theta/\nu_r$, on $f$ (horizontal axis) and on the ratio, $u$ (indicated by the dashed vertical lines). Fig. 4 shows some of the orbits for $u = 3$. The calculations were performed, using Princeton's IBM 7094 computers, by

numerical integration of Eq. (2) for various values of the power law exponent, $s$, and the apogee to perigee ratio, $u$. The value of $u$ can be preassigned before integration of Eq. (2), whereas the value of $f = J_r/(J_r + J_\theta)$ can be determined only after the orbit has been calculated. Then, in order to determine the dependence of the frequency ratio, $\nu_\theta/\nu_r$, on $f$, $f$ had to

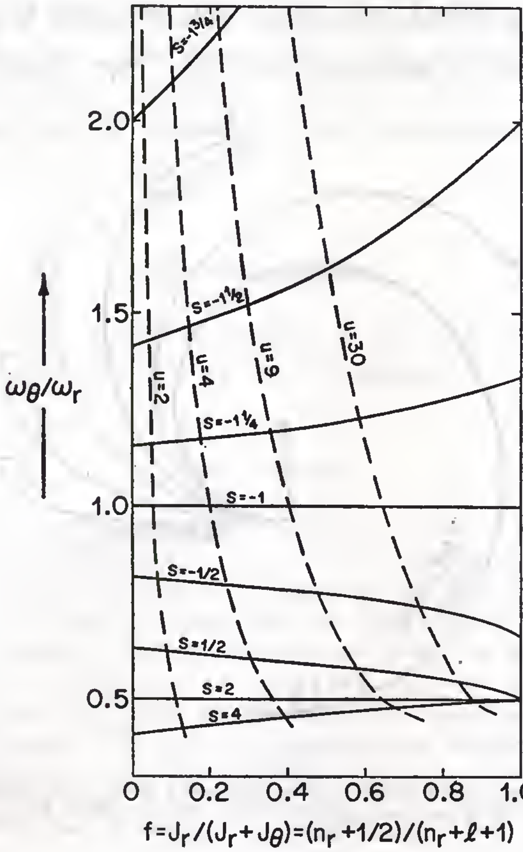


Fig. 3.

The frequency ratio, $\nu_\theta/\nu_r$, as a function of $f = J_r/(J_r + J_\theta)$ (horizontal axis) for various values of the power law exponent, $s$. The figure also shows the ratio, $\nu_\theta/\nu_r$, versus the apogee to perigee ratio, $u = r_{max}/r_{min}$, indicated by the dashed vertical lines.

be evaluated as a function of $u$. The angular action, $J_\theta$, is proportional to the angular momentum which is determined by $r_{max}$ and $r_{min}$. The radial action, $J_r$, was evaluated by numerical integration of the following integral around the closed orbit:

$$(3) \quad J_r/h = n_r + \frac{1}{2} = (1/2\pi) \oint \left[ (2m/\hbar^2)(E - V) - \left(l + \frac{1}{2}\right)^2 \Big/ r^2 \right]^{1/2} dr\,.$$

Then $f$ could be determined as a function of $u$ from a knowledge of $J_r$ and $J_\theta$.

For the extreme points, $u = 1$ and $u = \infty$, (or $f = 0$ and $f = 1$ respectively) the frequency ratio, $\nu_\theta/\nu_r$, can be evaluated exactly. For circular orbits, ($u = 1$) one expands the effective potential, $(2m/\hbar^2)V(r) + \left(l + \frac{1}{2}\right)^2 \Big/ r^2$, to second order in $r$ about the point $r_0$ (at which this expression takes on its minimum value). One then obtains a simple li-

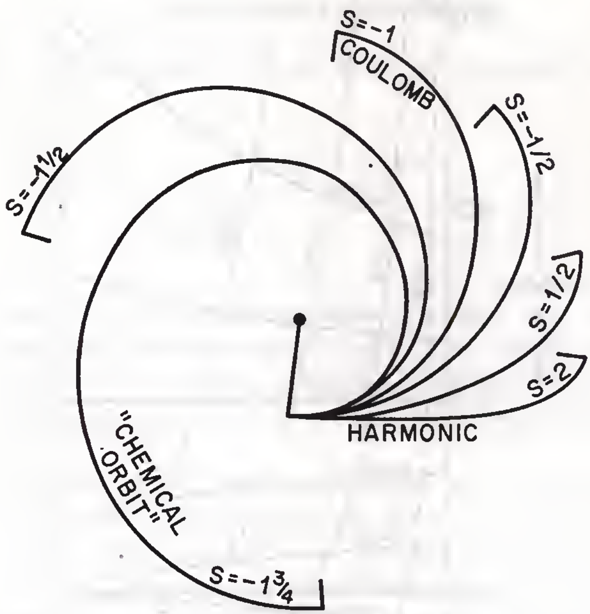


Fig. 4.

The orbits of a particle in a central potential, which varies as a power of the distance, are shown for various values of the power law exponent, s. The orbits are shown for $r_{max}/r_{min} = 3$.

near differential equation for the orbits perturbed slightly from circularity. One finds

$$\nu_\theta/\nu_r = (2 + s)^{-1/2} \tag{4}$$

For penetrating orbits ($u \to \infty$) one evaluates the integral obtained from Eq. (2) in the limit of $r_{min} \to 0$. One finds

$$\nu_\theta/\nu_r = \frac{1}{2} \qquad s > 0 \tag{5}$$

$$\nu_\theta/\nu_r = (2 + s)^{-1} \qquad s < 0 .$$

From Fig. 3 it can be seen that $\nu_\theta/\nu_r \approx 2$ for $-7/4 \leq s \leq -3/2$. One concludes that the effective potential of an atom, as sampled by an outer electron in the domain of shell filling, can be roughly approximated by a power law potential with exponent between $-7/4$ and $-3/2$. Moreover the « orbit » of such an electron, as described by the motion of a wave packet built out of nearby quantum states, looks approximately as illustrated in Fig. 2. We suggest this orbit be called « the chemical orbit » as a shorthand designation, provided that recognizes all the precautions that have to be taken against identifying this orbit with anything « real » in the atom.

## Acknowledgments.

The author is indebted to Professor J. A. Wheeler, who suggested this problem, for his guidance and encouragement.

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G. WATAGHIN (*)

# Relative Abundance of Elements in Cosmic Radiation.

The understanding of the Mendeleev periodic table required much experimental and theoretical work, mostly done in the XX century. The creation of quantum theory and the experimental discovery of new chemical elements and of many elementary particles allowed to find laws and models of atomic structure and illuminate some deep aspect of the periodicity of the Mendeleev table.

The purpose of the following remarks is to illustrate briefly the problem of the origin and of the distribution of chemical elements in the universe and the related question concerning the relative abundance of nuclei in the primary cosmic rays. Both problems concern obviously properties of the nuclei. Special consideration will be given to the recent finding of heavy transuranic elements in the cosmic radiation of galactic origin. In early 30th the great discovery of the similarity in the distribution of relative abundancies of elements on the earth, on the sun and on stars, and also in the cosmic radiation, induced the physicist to conclude that the formation of nuclei, their decay and their transformation in collision processes followed nearly the same historical evolution everywhere. Subsequent fundamental discovery showed the existence of the " weakly interacting black body radiation " of nearly 3 (°K) which fills uniformly the whole space. It is noteworthy that there are other types of particles filling uniformly the space. Let us recall that the cosmic rays can be classified in rays originated inside our galaxy and in " extragalactic " cosmic radiation which fills the whole space and contains particles of extremely hight energy (up to $10^{20}$ ev). Another group of particles, which fills the whole space is constituted by 4 types of neutrinos. These were created abundantly in an early epoch, and later have formed a practically noninteracting " neutrino phase ", homogeneous and isotropic.

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There are indications of the existence of still other types of radiation filling the universe: the extra-galactic X-rays and $\gamma$-rays and possibly the gravitons. All the above mentioned facts are in accord with the isotropy in the observed redshifts and the nearly isotropic distribution of very distant objects, like quasars or special classes of nebulae. Therefore, taking into account also the recent refined measurements of the red shift parameters (Hubble constant and deceleration), one is inclined to accept the Friedman model of an expanding universe, homogeneous and isotropic in each 3-dimensional subspace: $x_4 = \text{const.}$ Naturally one must approximate the actual inhomogeneous distribution of stars, radiation and galaxies, averaging it over some sufficiently large domains.

I shall not discuss here the speculations about the very early epoch of the expansion, near the singularity of the Friedman model. In the " physical " model this singularity presumably does not exist because particles have a repulsive core and all the fields must be quantized. The primeval state of matter at this epoch could be constituted of quarks or of even more fundamental particles of zero mass (like those considered by Heisenberg). I shall limit myself to assume that, at a certain early epoch, the universe was filled with all kinds of particles in a state of a very high density ($\sim 10^{14}$ gr/cm$^3$) and an extremely high temperature, presumably $T \gtrsim 10^{12}(°K)$. Thereafter instabilities, like the gravitational instability, gave rise to the creation of quasars, galaxies, stars, nuclei and to the separation of matter and anti-matter. It seems noteworthy that the evolution of the actual world, as we see it, follows often statistical laws (due to the great number of particles), and that the fluctuations and inhomogeneties are superimposed on the regular expansion described by the Einstein equations.

Let us consider our own galaxy and examine the problem of the relative abundancies of nuclei in stars and in galactic cosmic rays. These galactic rays originate in some stars (partly in our sun). Some of them are produced in super-novae explosions. The surprising discovery that the relative abundance of heavy nuclei in galactic cosmic rays differs from the average abundance everywhere in the universe deserves special attention. The most remarkable result was obtained recently by P. Fowler, who observed (with special apparatus exposed to primary cosmic rays by means of baloons at high altitude) several examples of incoming trans-uranic nuclei having an atomic number $\sim 110$ or $\sim 114$. These high energy nuclei could come only from our galaxy and, in order to arrive to the earth surface, travelled probably millions of years. Thus they have a considerable lifetime.

The most plausible origin of these transuranic nuclei, which were not yet produced in the laboratory, can be sought in the pulsars (G. Silvestro, 1969). Indeed, whereas the light nuclei are produced in some thermodynamical processes, the heavy nuclei are presumably produced by a successive capture of neutrons. Pulsars are neutron stars of extremely high density ($\sim 10^{14}$ gr/cm$^3$). One can imagine that near their surface the conditions are favorable to the creation (by a rapid capture of many neutrons), of transuranic nuclei belonging to a new family having, e. g., the magic number of protons = 114. The emission of these nuclei could take place because some of them could be accelerated in the strong electric and magnetic fields existing on the surface of the pulsars. The whole question needs naturally further experimental and theoretical research.

# Three Steps in the Structure of Matter.

## I.

A hundred years ago Dimitri Ivenovich Mendeleev discovered the periodic table of elements. He found striking periodicities in the chemical and physical properties of the elements when they were ordered according to their atomic weight. These findings for the first time brought some order into the chaos of elements; it is one of the greatest empirical discoveries in science. These mysterious regularities presented a great challenge to generations of scientists; obviously the explanation would be intimately connected with an insight into the structure of the atom. It took 52 years and much of new physics before Niels Bohr was able to unravel this riddle in his famous publication on the « Aufbauprinzip ».

In this lecture I would like to compare this achievement with two other similar developments in more recent stages of our recognition of the structure of matter. I have in mind the shell model of nuclei which brought order into the chaos of 270 nuclides by discerning a periodicity in the nuclear properties. It was found by J. H. D. Jensen, M. G. Mayer, O. Haxel, and H. E. Suess in 1951. The other development is the scheme introduced by M. Gell-Mann and K. Nishijima which brought some order into the chaos of the long list of so-called elementary particles which were discovered in the recent decades. Together, these three developments represent three decisive steps in our recognition of the nature of matter. We have found a clear explanation of the observed regularities in the first and second case; in the third, however, the explanation is still outstanding; the task is not accomplished.

## II.

Let us return to the first step whose 100th anniversary we celebrate today. It was the most important one of the three since the first step is always the hardest. In the 19th century Physics and Chemistry were

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separated disciplines. Chemistry dealt with « unphysical » concepts such as indivisible atoms with definite and unchanging characteristic shapes and qualities - concepts which had no place in contemporary classical physics. The physics of that period dealt with continuously variable qualities of solids, liquids, or gases which were governed by material constants, such as elasticity coefficients, viscosities, dielectric properties, conductivities, etc. Physics did not consider its task to explain the actual values of these constants; its aim was to find the consequences in the behavior of matter for a given arbitrary set of values. The physics of the 19th century had no way to deal with the atom and its properties. It is true that the electron was discovered and its important role within the atom was suspected in the works of J. J. Thompson and H. A. Lorentz and their contemporaries. However, the two physical magnitudes associated with the electron — its charge $e$ and its mass $m$ — do not determine a length nor an energy. The quantum of action $h$ was needed which was introduced by Planck's great contribution in 1900.

The quantum theory is a child of the 20th century. The year 1900 is not only a round number, it is the key year of a revolutionary change in physics which culminated in a « physicalization » of the chemical concepts. The stability of atoms, their sizes and excitation energies became objects of physical reasoning. Quantum mechanics proved a basis for a rational understanding of chemical phenomena. It gave rise to atomic units of length and energy, the Bohr radius and the Rydberg. They result from a balance between the Coulomb-attraction of electrons by atomic nuclei, and the quantum mechanical zero-point energy of electrons in a confined region of space. It introduced into physics a « morphic » element: the fundamental equations of quantum mechanics give rise to characteristic shapes and patterns which reflect the intrinsic symmetry of the atomic or molecular situation.

The spatial arrangements of chemical bonds has found its physical explanation. Finally the logical existence of discrete and well-defined quantum states gave the conceptual basis for the observed stability and unchangeability of chemical properties. The properties of quantum states are to a large extent determined by their symmetries and by a set of quantum numbers determining these symmetries. Thus, the chemical ideas and concepts turned out to be contained in quantum physics. Chemistry has ceased to be a separate science.

The quantum theory of the atom was the basis for Niels Bohr's explanation of Mendeleev's periodic system of elements. The modern reader is surprised how Bohr could anticipate the correct explanation in 1921, before the formulation of quantum mechanics and — even more surprising — before the recognition of the exclusion principle which Pauli

found in 1925. Bohr constructed his atoms one by one by adding one electron after the other to the elements. His force of intuition was so great that he divined the fact that not more than two electrons can be placed in one orbit, which almost automatically leads to the periods of Mendeleev. He was able to read this fact from the properties of atomic spectra; he saw it before his mental eye when studying the Mendeleev periodicities. He tried hard to understand the double occupancy of orbits by talking about « a disinclination to accept more electrons with the same quantum numbers » or that « electrons with the same *m* and *k* are possible only if they form a harmonious interplay ». The great critic and puritan Wolfgang Pauli, did not like these attempts of an explanation. He sensed already in 1921 that there was a major principle hidden in these regularities. As an interesting testimony to Pauli's attitude, I quote some remarks which I found scribbled on the margins of a book containing Bohr's paper, belonging to the Pauli library at CERN. This paper contains the following statement, when the adding of the eleventh electron to the closed shell of 10 electrons is discussed: « We must expect the 11th electron going in the third orbit ». Pauli obviously is annoyed by this and writes hastily in the margin with two exclamation marks (non-literally translated): « No reason to expect anything, you concluded it from the spectra! » (1).

Four years later, after careful analysis of atomic spectra and of the Zeeman effect at high fields, Pauli was able to formulate clearly his exclusion principle. Bohr's explanation of the periodic system of elements was put on a firm basis. The exclusion principle turned out to be one of the most important principles added to the basic ideas of quantum mechanics. It provided the foundation to almost all quantum mechanical explanations of the behavior of matter. Fifteen years later, in 1940, Pauli could prove that the exclusion principle for particles with half integer spins is not an added new principle, but it follows necessarily from the structure of relativistic wave equations.

Quantum mechanics has incorporated chemistry into physics. The concepts of chemistry are no longer « unphysical ». Quite to the contrary, they follow directly from the fundamental tenets of quantum theory. A most important step towards the unity of sciences was taken: the various interactions between atoms which were expressed in terms of chemical forces, van de Waal's forces, adhesion, viscosity, electricity, capilarity, etc., were all reduced to one well-known natural interaction: the electro-

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(1) Bohr's sentence: « Wir müssen erwarten dass 11. Elektron (Na) in die 3. Bahn geht ». Pauli's remark: « Wir ' müssen ' es nicht ' erwarten ' aben wir wissen es aus den Spektren! ».

static attraction between electrons and nuclei, whose effects are modified according to the circumstances by the laws of quantum mechanics.

I wish to point out that the quantum mechanics of atoms and molecules is governed by two fundamental numbers whose small value are essential for the character of the observed phenomena: the fine structure constant $e^2/hc$, and the mass ratio between electron and nucleon $m/M$. If $e^2/hc$ would be near unity or larger, atomic mechanics would be dominated by relativistic effects, such as electron-positron pairs as important constituents of atoms. Physics and chemistry would be completely different. The smallness of the mass ratio $m/M$ is responsible for molecular structure: The average distance between nuclei in a molecule is determined by the size of the electron orbital, a length which can be considered as the amplitude of the zero-point motion of electrons. The nuclei are subject to the same force (Newton's third law) but their zero-point motion is reduced by a factor $(m/M)^{1/2}$. Thus they are well localized within the molecule. They form a nuclear skeleton which makes possible the immense variety of molecular architecture, including crystals and macro-molecules. If the mass of the proton were of the same order as the electron mass, there would be no chemistry, no solid bodies, and, in the last instance, no life and no mind to consider the problem. The reason for this difference of mass is still unknown. It certainly is connected with the existence of strong interactions between nucleons, and it is one of the central problems of modern particle physics. As long as we do not understand the origin of the heavy mass on nucleons, we cannot claim to understand the basic reasons why the world around us is the way we observe it. The electron-proton mass ratio and the value of the electric charge measured in unit of $hc$, are two fundamental numbers which determine the properties of matter; we still are ignorant of the reasons for their smallness and for their actual values.

## III.

Our world of chemistry and biology can only exist in an environment where energy exchanges between particles are not too violent and where enough energy is available to initiate non-violent changes in molecular structure. These benign conditions are available on earth because of the safe distance of $10^{13}$ cm from a regular star and of the protective cover of an atmosphere. Most of the matter in this universe exists under very different conditions. In the center of the stars, for example, another world of phenomena is of prime importance: the world of nuclear processes. This is the realm in which the second ordering principle is relevant. On the surface of the earth nuclear phenomena are practically non-existent.

The energies available are not sufficient to initiate them. We find rare cases only, of such processes, the natural radioactive elements, which are then long-lived remnants of a distant past when terrestrial matter probably was ejected by a supernova explosion. In order to study these phenomena in our laboratories we have to produce them with particle accelerators. These studies have been highly rewarding since they have

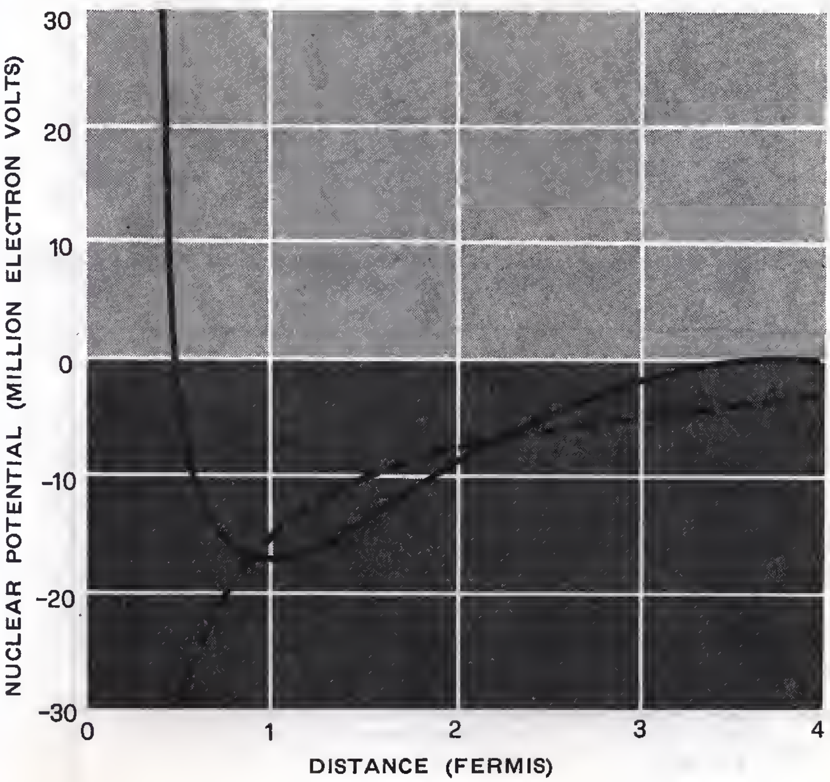


Fig. 1.

The potential of the force between two nucleons. The solid curve is an approximate rendition of this potential. The exact value depends on the relative spin direction of the nucleons and on the symmetry of the quantum state. The broken line indicates the electrostatic potential between two particles of opposite charge, 3.3 times the charge of the electron.

uncovered the existence of a world of phenomena so different and yet so analogous to our atomic and molecular environment. First of all, a new force was discovered. It acts between the nucleons, the protons, and neutrons. It is turning out to be a complicated force (see fig. 1). Repulsive at very short distances of less than $10^{-13}$ cm (a «fermi» unit) it becomes attractive in the region roughly between one and several fermi's and goes exponentially to zero at larger distances. Moreover, the details

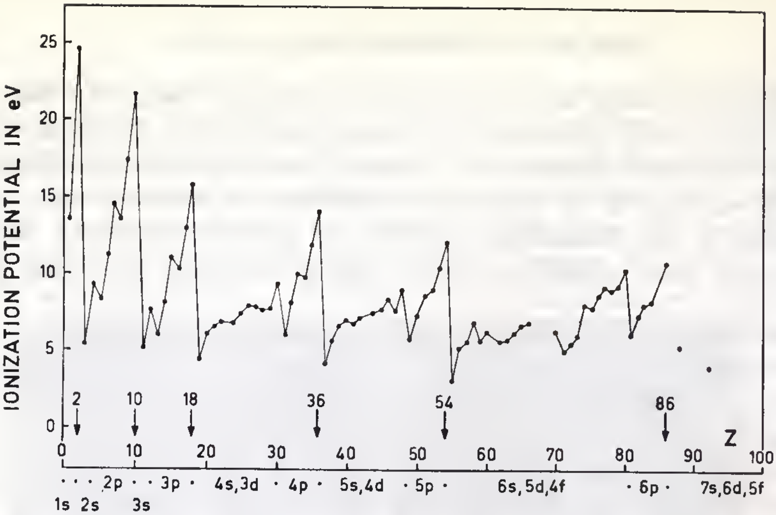


Fig. 2.

Ionization energies of atoms as a function of number of electrons. (From Bohr and Mottelson, *Nuclear Structure*, New York, 1969).

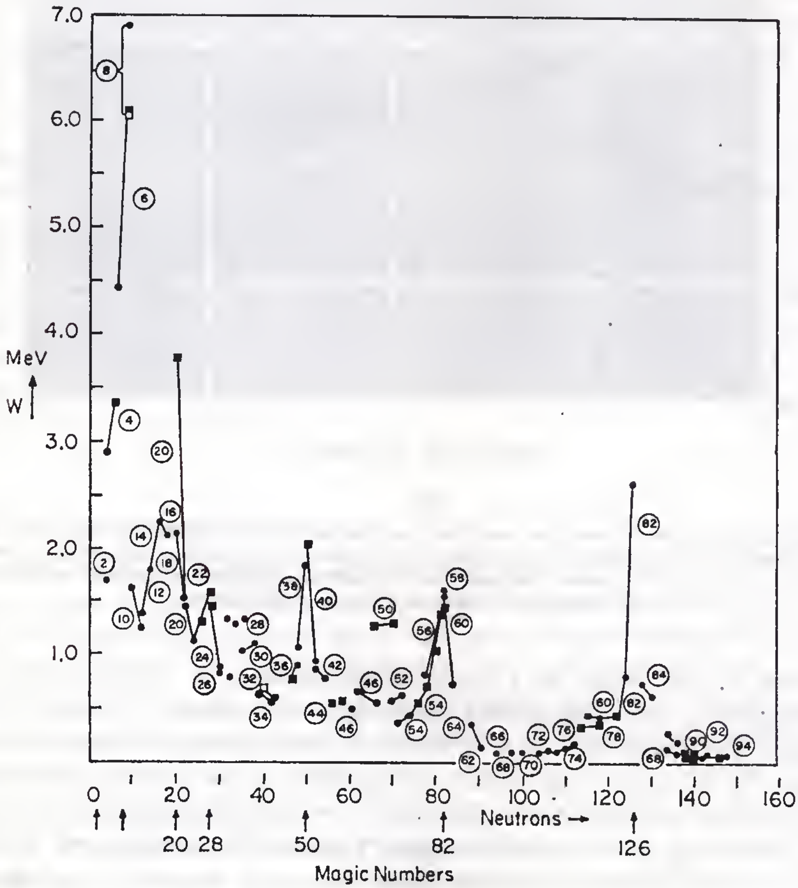


Fig. 3.

The excitation energy of the first excited states of nuclei as a function of number of neutrons. (From G. S. Goldhaber, « Phys. Rev. » 90, 589, 1953).

depend on relative spins and symmetry of the quantum state of the two particles. Because of the short range of this force, it is not possible to produce a large nuclear force-strength by concentrating many nucleons, as one can do with electric charges in order to produce large electric fields. The strong repulsion at small distances makes it impossible to assemble a large number of nucleons within a volume of the linear size of the range.

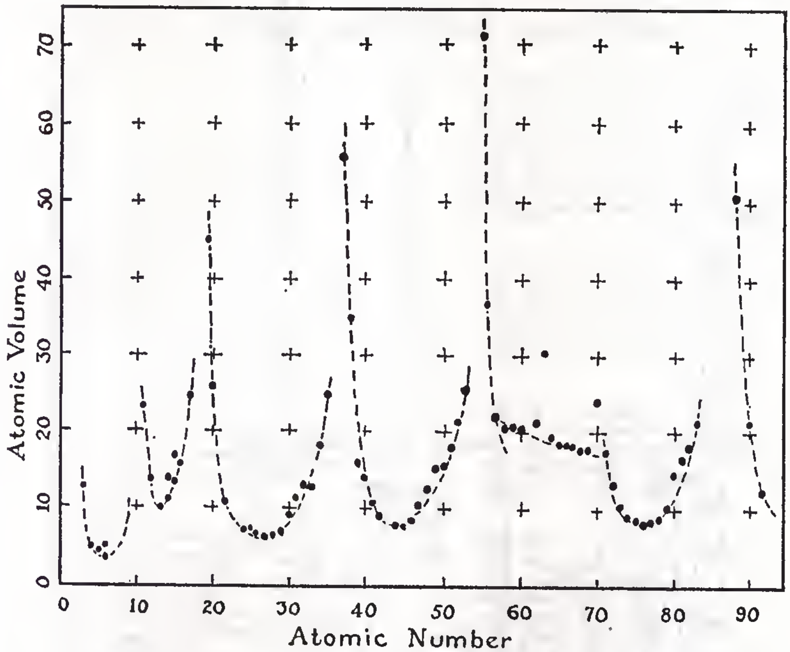


Fig. 4.

Atomic volume as function of number of electrons. (From L. Pauling, *General Chemistry*, San Francisco, 1959).

There is no macroscopic analogue to the nuclear force. The approximate strength of nuclear force in the attractive region can be expressed by stating that, in this region, it is comparable to the attraction between two opposite charges of magnitude $3e$. This value allows us to estimate the energies and sizes of simple nuclei. They should be given by the well-known expressions for the Rydberg and the Bohr-radius, but $e$ should be replaced by $3e$, and the electron mass by the nucleons mass. Then nuclear energies become 200.000 times larger, nuclear sizes 20.000 times smaller than the corresponding atomic magnitudes.

In many ways nuclear physics turned out to be a repeat performance of atomic physics with similar spectra and quantum numbers. There are characteristic differences, such as the absence of an overriding field of

force originating from a heavy central particle, and the different nature of the nuclear force, producing an effective attraction between all con-

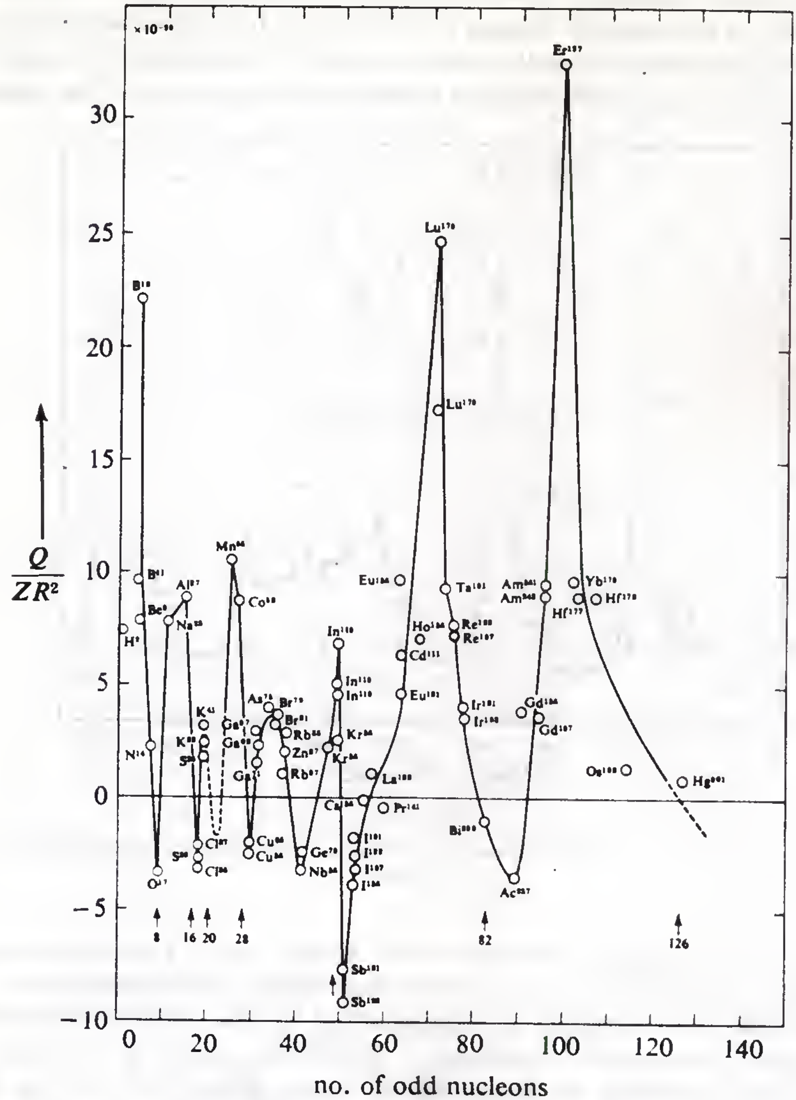


Fig. 5.

Quadrupole moment as function of number of odd nucleons. (From E. Segre, *Nuclei and Particles*, New York, 1964).

stituents. In quantum mechanics, however, the symmetry of the situation is a determining factor in regard to many properties. The average attractive field to which each nucleon is subjected has the same spherical sym-

metry in atoms as in nuclei. Hence we obtain similar sets of quantum numbers, a similar « Aufbau » principle, a similar periodic system of nuclear properties, when the nuclei are ordered according to the number of protons or neutrons. We find nuclei with closed shells and high binding energies at the end of the periods, the « magic » nuclei, which correspond to the inert gases. Figs. 2 and 3, 4 and 5 compare nuclear periodicities with

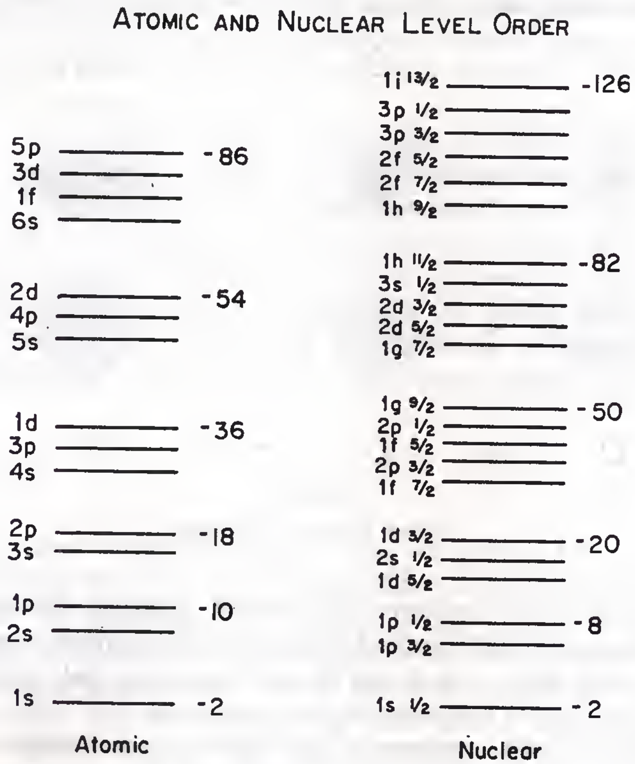


Fig. 6.

**Atomic and nuclear one-particle-levels order. This figure indicates the approximate order only, not the energy-values. The figures on the right give the numbers of particles which would fill the levels up to the line preceeding the number.**

corresponding atomic ones; in the first case atomic ionization energies with nuclear excitation energies, in the latter, atomic volumes with nuclear quadrupole moments. The general character is similar, but there are important deviations.

First of all, the order of levels in the average potential of the nucleus is different from the order in a Coulomb field (see fig. 6); the former has no singularity in the center, the 2*s* level is higher than the 1*p* level, where as in the latter case the order is reversed. Second, a strong spin-orbit

coupling in the nucleus changes the occupation numbers of successive shells such that the ends of periods occur at different particle numbers. Moreover, in atoms there is a repulsion between the electrons; in nuclei there is attraction between all constituents. This difference brings about a reversal of Hund's rule in nuclei: This rule maintains that the atomic ground state is the state of highest multiplicity of the configuration in the last incomplete shell, since in that state the electrons stay apart from

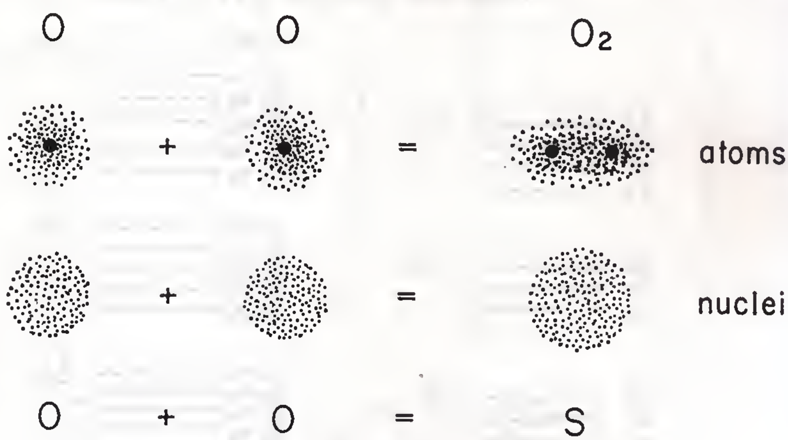


Fig. 7.

Atomic and nuclear reaction.

each other. In nuclei, however, the ground state has the lowest multiplicity. The lowest multiplicity for any even occupation number is zero. Hence all nuclei with even $Z$ and $N$ have zero spin. Only odd occupation numbers give rise to non-zero angular momenta.

Furthermore, the existence of two types of constituents — neutrons and protons — of almost equal weight bring about interesting effects. The two types are fully equivalent in regard to the nuclear force. Hence there is an approximate degeneracy of quantum levels which differ by replacing a number of neutrons by protons. The degeneracy is broken only by the weaker electric effects coming from the protonic charge. This degeneracy gives rise to a new approximate symmetry in regard to proton-neutron exchanges and to a new quantum number, the isotopic spin, which governs nuclear spectra. Another consequence of equal mass among constituents is the absence of any special localization among them. There is no well-defined center within the nucleus. Hence when two nuclei merge in a nuclear reaction, the product is not a « molecule » but a new nucleus: Two merging oxygen nuclei would give a sulfur nucleus (fig. 7). There is no skeleton or superstructure formed. In this sense, the possibilities

of creating new structures by combination is much poorer with nuclei than with atoms. However, the energy released in nuclear mergers is $10^6$ times larger than in chemical reactions. This is what keeps the sun bright and warm for thousands of millions of years.

Also, there is an upper limit for the number of nucleons which can be joined, because of the increasing disruptive effect of the Coulomb repulsion. It is possible that some special shell-effect may extend this limit further than the presently known transuranic elements. Also, in the large, the gravitational attraction would help keep nucleons together, as in the recently discovered neutron stars.

Another new feature appears in the nuclear world. Transitions between quantum states from higher to lower energy take place not only by emission of light quanta as in atoms but also by emission of lepton pairs — electrons and neutrinos. These emissions are manifestations of the mysterious weak interaction; they exhibit surprising properties, such as a violation of the right-left symmetry. They permit transitions between states of different total charge, thus allowing a nuclear system to find its ground state with that number of protons which minimizes the energy.

## IV.

We now come to the third step in the recognition of the nature of matter. It is the penetration into the structure of the nucleon itself, and the new realm of phenomena discovered hereby. The nucleon turned out to change its state when bombarded with very energetic particle beams of energies larger than several hundred million electron volts. One observes that the nucleon assumes short-lived «excited» quantum states, from which it returns to its ground state (neutron, proton) with the emission of the energy difference in various forms. The spectrum of these «excited» states is shown in fig. 8. It is seen that the energy differences are of the order of several $10^8$ eV, about 1000 times larger than excitation energies of nuclei. When these phenomena were discovered, the excited states were not yet put in this well ordered array. One state after the other was found and considered a new elementary particle. After careful study of the excitation energies quantum numbers and the emission products, M. Gell-Mann, K. Nishijima, Y. Ne'emann and many others were able to unravel the apparent chaos of large numbers of elementary particles, and put order into it, by introducing a new quantum number (the «strangeness» or hyper-charge), and by a group-theoretical classification ($SU_3$). The new particles named with many Greek letters — the $\Delta$-, $\Sigma$-, $\Xi$-, $\Omega$-particles — were recognized as excited states

of the nucleon which fall into distinct groups, each of which is characterized by the values of certain quantum numbers. These numbers are partly of the variety known from atomic and nuclear physics, such as

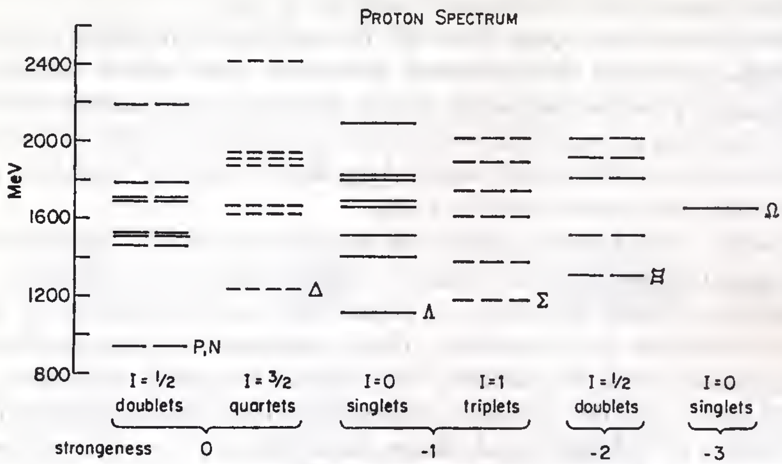


Fig. 8.

The spectrum of the excited states of the proton.

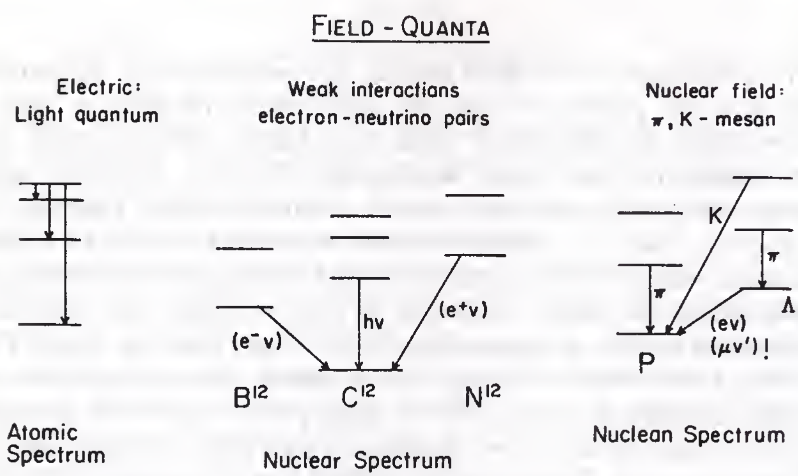


Fig. 9.

The field-quanta emitted in the three types of spectra.

angular momentum and isotopic spin; but a new quantum number, the above mentioned hypercharge, made its appearance.

Another important aspect of this new realm of phenomena is the appearance of a new form of energy emitted or absorbed when the nucleon

performs a transition from one quantum state to another. Light quanta and lepton pairs are emitted just as in atomic and nuclear systems. Adding to the mysteries of weak interactions, a new lepton appears in these transitions: The heavy electron, being about 200 times heavier

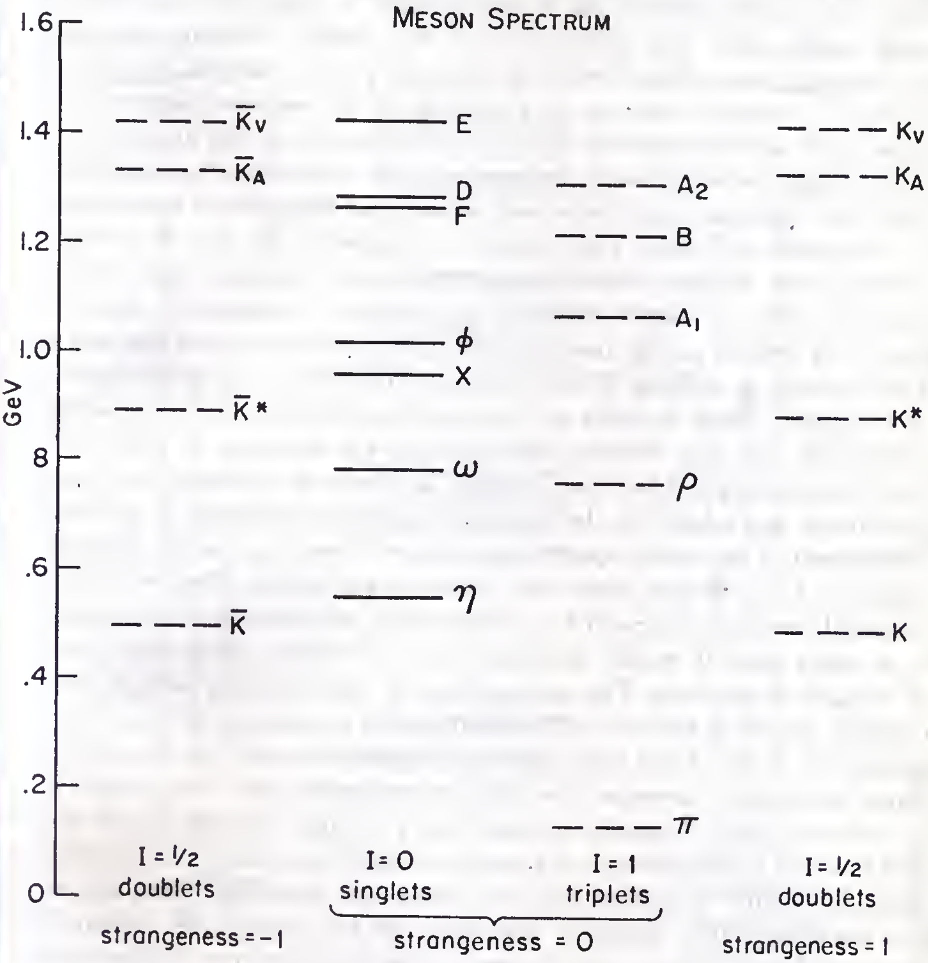


Fig. 10.
The spectrum of mesons.

than the ordinary one. But the really new forms of energy emitted and absorbed are the mesons (see fig. 9). There exists a large array of different mesons — a spectrum of mesons — which also can be classified and grouped according to the same quantum numbers used for the nuclear spectrum. (see fig. 10). Indeed, in a change of a nucleon state, the difference in quantum numbers is delivered or removed in the acts of meson absorption

or emission. Thus the classification according to quantum numbers also brought order into the chaos of meson states.

Here we are facing a third spectroscopy, a third system of excited states with its own rules and regularities. The atomic spectra were the first, the nuclear spectra the second system. Let me, at this point, cast some doubt upon the justification of this trinity. Perhaps one should not consider the nuclear spectra as an equal partner here. It may be more logical to consider them as an extension of the *nucleon*-spectrum in the same sense as the molecular spectra are extensions of the atomic spectra. The analogy between nuclei and molecules is understood in the following way: The nucleons play the role of atoms, and the nuclear forces the role of the chemical forces. This analogy is reinforced by the fact that the nuclear force exhibits similar properties as the chemical one. They are both attractive at larger distances and strongly repulsive at short ones; they both depend on the relative spins and the symmetry of the partners. The analogy is striking if one considers the wider excitation spectrum of a nucleus, which includes not only the excitation of the proton-neutron system but also the internal excitations of the nucleons as given by the third spectroscopy. One then obtains a spectrum in which the nuclear excitations are added to the internal nucleon excitations. It is strongly reminiscent of molecular spectra (see fig. 11). There are certain differences, however. In a certain sense the nuclear force is less effective than the chemical force as witnessed by the fact that the binding of the deuteron is so weak that it would dissociate even if rotating with one quantum of angular momentum. The nuclear force is barely strong enough to concentrate the wave function of the deuteron in the ground state sufficiently within the range of the force such that binding ensues. The bonds of diatomic molecules, however, are able to withstand the centrifugal force of 20 to 40 units of angular momentum. The same contrast is seen in the fact that the binding energy of a nucleon within the nucleus is much smaller than its internal excitation energies, whereas in molecules these two energies are comparable. Probably it is more apt to compare the nuclear force with the Van-de-Waals force between closed-shell atoms. Nuclear matter would then correspond to superfluid helium, an analogy which goes surprisingly far in explaining the relatively independent motion of nucleons within the nucleus (shell model) and some typical properties of the spectra connected with a phenomenon corresponding to the energy gap of a superfluid.

Whatever way one looks at it, the rather complicated form of nuclear forces makes it tempting to assume that the nuclear force is not a fundamental force such as the electrostatic attraction. It may be a derived effect of a more basic phenomenon residing within the nucleons, a con-

sequence of something much more powerful and simpler, in the same way as the chemical force is a consequence of the simple electric interactions of electrons and nuclei.

Let us return to the excited states of the nucleons and the mesons. In contrast to the atomic and nuclear realm, the order found in this thir

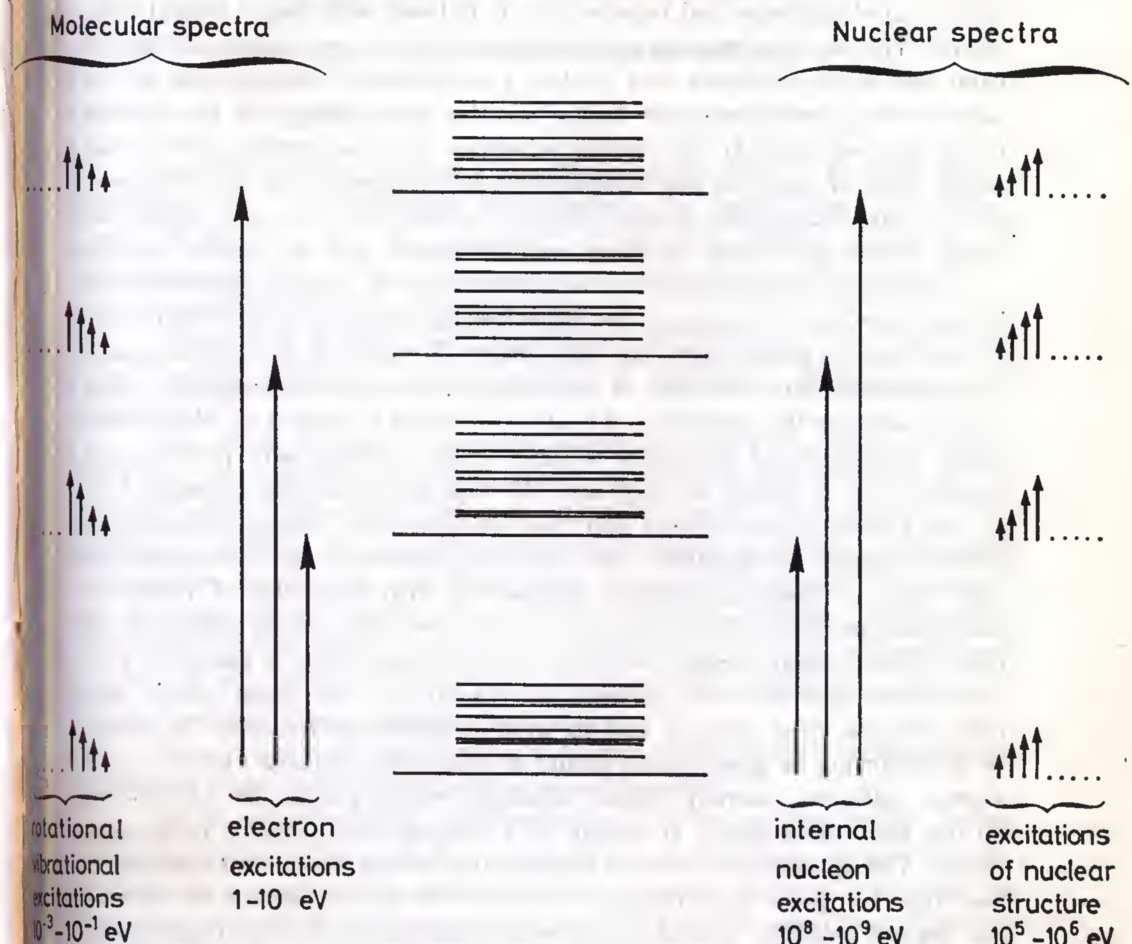


Fig. 11.

Schematic sketch of a molecular spectrum and of a nuclear spectrum. The arrows at the left indicate the nature and energies of the levels in molecules, the ones at the right refer to nuclei.

spectroscopy so far is empirical. It cannot be explained or derived from the internal dynamics of the system because this dynamics is largely unknown. One feature of this order is most intriguing. The spectrum of the nucleon and of the mesons exhibits certain features which point toward a composite structure of these entities. The nucleon spectrum has some

of the characteristic properties of a three-particle system, where each particle is a member of a typical triplet of some subparticles of half-integer spin. The meson spectrum looks like a spectrum of a pair of those particles, or, rather, of a pair of a particle and its antiparticle. This so-called « quark-model » can explain a large amount of phenomena connected with excited nucleons and mesons, but it is beset with many logical difficulties. The world of mesons and nucleons differs in one important aspect from the world of atoms and nuclei: The excitation energies are of the same order (sometimes even larger) as the mass energy of the system in the ground state. If the relevant energies of these systems are in that range, pairs of particles and antiparticles will be present or virtually present in any interaction process. This is a new and essential feature of these entities for which we have no systematic way of dealing as yet.

The structure of nucleons and mesons is still largely unknown. We do not know what determines the forces between them, and why the energy of the nucleon-groundstate has the observed value of the proton mass. We remember that the value of this mass in relation to the electron mass was decisive for the properties of matter as we see it around us. We cannot claim to understand chemistry without understanding why protons and neutrons are as heavy as they are. We are just beginning to learn how to speak about these objects and their interactions. Dispersion relations, current algebra, Regge-poles are ways and means to put the observed facts into a logical framework, compatible with the rules of relativity and quantum fields. Most probably it will be necessary to make use of much higher beam energies before we can find out what is going on « inside » these structures. At present, all we do is to let them collide and find out how they interact and in what quantum states they fly apart. It is like trying to guess the structure of atoms by studying « low energy » atomic collisions, namely, those collisions which excite the atoms but do not take them apart. It would be a difficult, and perhaps futile operation. The spectrum of excited nuclear and meson states was discovered less than ten years ago. There is no reason to be despondent in view of our present inability to understand what underlies its strange regularities. It took fifty-two years to find the explanation of the regularities discovered by Mendeleev.

N. N. BOGOLUBOV (*)

# On Superfluid Nuclear Model.

Nuclear physics originates from the establishment of the Mendeleev's periodic law. The Mendeleev Table reflects the regularities of the structure of the atom and the importance of the mass number $A$ and the nuclear charge $Z$. In the development of nuclear physics the periodic law has played the role of a leading idea.

Complexity, richness and diversity of the properties of atomic nuclei are the main physical reasons why it is difficult to formulate nuclear theory.

Two main difficulties are encountered in formulating nuclear theory. Firstly, the forces acting between the nucleons in the nucleus have not been studied sufficiently and are extremely complicated; secondly, even when simplifying assumptions about these forces are made, considerable difficulties arise in the study of the properties of a system consisting of a large but finite number of strongly interacting particles. It should be stressed that in the system under consideration there is no small parameter in which to make an expansion to give the solution for the many-body problem using perturbation theory.

Consequently, in constructing a theory of the nucleus, physicists have directed their effort to developing simple models.

At the initial stage of the development of nuclear physics the nucleus was described by the liquid-drop model or the Fermi-gas model. Further, the term « model » was understood in a broader sense of this word. In modern nuclear theory the model is taken to mean an approximate method for the study of nuclear properties which takes into account the most important part of nuclear forces.

In the development of nuclear physics, of great importance are the shell model and the unified nuclear model. Thus, using the shell model, one has succeeded in explaining not only a special stability of magic nuclei but also a large amount of experimental data on the properties of the

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ground and excited states of nuclei and a number of the particular features of their decay.

The phenomenological description of nuclear structure is performed in the framework of the unified model. In the phenomenological description of the structure of complex nuclei, collective co-ordinates are introduced and the nuclear excitations are considered to be due to the rotations of the nucleus as a whole and to the nuclear surface vibrations. Each nucleus is characterized by several parameters. The energy of the excited states, their multipole moments and the probabilities of electromagnetic transitions are expressed in terms of these parameters. The values of the parameters are determined from the corresponding experimental data and characterize the properties of a given nucleus.

The development of nuclear physics has led to the appearance of a number of experimental facts which could be explained by neither the shell nor the unified model. These are, for example, the presence of the gap in the excited state spectra due to the change of the intrinsic structure in even-even nuclei and its absence in odd-mass nuclei. The moments of inertia calculated by the independent particle model were found to be larger than the experimental ones by a factor of two or three.

The moments of inertia of odd nuclei are noticeably larger than those of the neighbouring even-even nuclei. The fact that this difference exceeds by many times the contribution of one nucleon shows that this effect is due to a change in the properties of the many-body system.

Great difficulties have appeared in explaining the equilibrium nuclear shape. Some peculiarities of alpha and beta decays have not been accounted for at all. A considerable improvement of the description of vibrational states was needed.

A large number of unexplained experimental facts, essential difficulties of the pure phenomenological theory, and any attempt to explain vibrational states starting directly from the nucleon interaction Hamiltonian, made it necessary to develop a new approach in nuclear theory which is commonly called the semi-microscopic model. This approach is connected with the choice of the effective nuclear interaction. The most important part of the force is found for each nuclear phenomenon and is described mathematically. This semi-microscopic trend is a natural development from the phenomenological model. Its success is due to the fact that in studying nuclear structure we restrict ourselves to the lowest excited states. Therefore the many-body problem reduces to the problem of a small number of degrees of freedom.

This approach grew directly out of our understanding of the theory of superconducting pairing correlations. Investigations on superfluidity [1]

and superconductivity [2, 3, 4] have played an important role in the development of this approach.

Let us say a few words about superfluidity of Bose-systems.

Consider first the simplest case when there is no interaction so that all bosons are independent.

As is well known, for sufficiently small temperatures the ideal Bose gas admits the so called « condensate ». In the lowest energy level all particles have zero momentum.

Even when the temperature $\theta$ is different from zero, being less than some critical $\theta_{cr}$, a finite fraction of particles are at rest in the condensate. Such a system has no property of superfluidity. Really let us imagine it moving as a whole in a tube with a certain velocity.

Nothing would prevent the particles under consideration from losing their momenta, e.g. by collisions with the walls, so the ideal Bose gas can not be superfluid.

In order to obtain a dynamical system exhibiting this property, we considered, some 23 years ago, the system of Bose particles with interaction. In this case the situation may become quite different even if the interaction is small.

There is still a condensate but the low lying excitations have no individual character.

Let

$$b_k, \; b_k^+$$

be Bose quantum operators describing annihilation or creation of momentum $k$.

These amplitudes describe the elementary excitations for the ideal Bose-gas. When the interaction (mostly of repulsive type) are taken into account it is profitable to make a change in quantum operators:

$$\beta_k = u_k b_k + v_k b_k^+ \tag{1}$$

where $u_k$, $v_k$ are real number subject to the condition

$$u_k^2 - v_k^2 = 1$$

which guarantees the canonical character of our transformation, and defined by some specific equations.

The elementary excitations are described now not by $b_k$, $b_k^+$ but by $\beta_k$, $\beta_k^+$. The energy of such elementary excitations has the form:

$$E = E(K)$$

schematically represented in fig. 1. It is easy to see that in this situation we shall have the property of superfluidity. Indeed, let us imagine that our system moves as a whole with a velocity $n$.

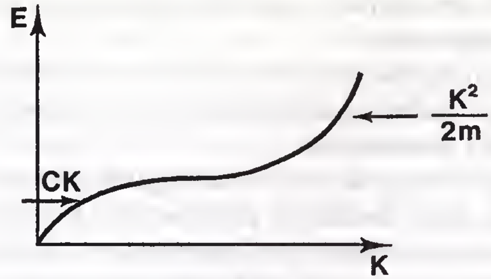


Fig. 1
($C$ is the velocity of sound).

Then the elementary excitations will have the energy:

$$E = E(K) - (\vec{K}\vec{n}) .$$

For a sufficiently small $n$ these energies will be positive (see the scheme of fig. 2) and, due to this fact, in order to create elementary excitation we must add the energy.

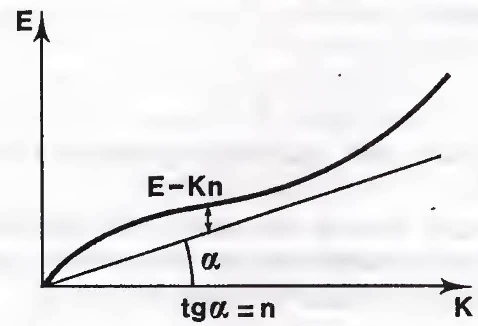


Fig. 2.

Hence we have the property of superfluidity — the flow is stable with respect to the creation of the elementary excitations. It is useful to note that for the ideal Bose gas

$$E(K) = \frac{K^2}{2m}$$

and the elementary excitations of the moving gas

$$E - (\vec{K}\vec{n}) = \frac{K^2}{2m} - (\vec{K}\vec{n})$$

will be negative for some small $k$ so that the stability of the flow will not be guaranteed. I wish also to mention here the property of the superfluid system. When this system is rotating only a part of it («normal part») takes part in the rotation, the other «superfluid» part staying at rest.

For this reason the moment of inertia of the considered system has a smaller value than for the «normal» case.

We have considered as yet only the Bose-systems. Now let us turn to the problem of superfluidity of systems of fermions.

The first most important application is the case of electrons in metals — the superfluidity of conduction electron being in fact the superconductivity. It is interesting to note that the theory of superfluidity of fermion systems could be elaborated using the same method as for Bose systems.

Let $a_f$, $a_f^\dagger$ be the destruction and creation quantum Fermi operators corresponding to

$$f = (\vec{p}, \sigma)$$

where $\vec{p}$ is momentum and $\sigma$ the spin.

Then all we have to do is to introduce new Fermi operators

$$\alpha_f, \ \alpha_f^\dagger \tag{2}$$

$$\alpha_f = u_f a_f + v_f a_f^\dagger$$

canonical character being guaranteed by the relation:

$$|u_f|^2 + |v_f|^2 = 1 \, .$$

The numbers $u_f$, $v_f$ may be calculated using some kind of the principle of compensation of dangerous diagrams by a sort of a minimum principle.

In such a way one may obtain in the first approximation essentially the same results as in the *B.C.S.* theory [2]. I wish now to say a few words concerning the physical picture behind the considered change of variables.

For the considered Fermi systems there exists also *a condensate*, like that in Bose system, formed by pairs of fermions. Because each of such pairs is at rest two particles forming a pair have opposite momenta and because they have not a total spin the spins of these particles are antiparallel.

I wish to stress that the idea that fermion systems may become superfluid when there is a possibility of forming a condensate out of pairs of

fermions is a long standing one. As far as I know it was first published a long time ago by the late prof. Schafroth [5].

In general this idea is quite correct. But in developing this idea, an oversimplified approach to the notion of pairs as molecules was used. When speaking about molecules, we must bear in mind that, if it is possible to use such an oversimplified and somewhat naive picture of the partners of a pair staying bound to one-another for all time, the exchange between partners of different pairs is not taken into account.

In the « condensate » of « pairs » we consider in the superfluid Fermi systems quite another picture — the partners of pairs are continuously exchanging their energies.

Physically, here the exchange energy is of the same order as that of the binding energy. In fact, the condensate of pairs is really a collective phenomenon.

Two types of excited states, excitations which break a pair creating two Fermi particles (such excitations have an energy gap), and collective excitations of the « phonon type » are considered.

It is also to be noted that a superfluid rotating system has a smaller moment of inertia because only a « normal part » takes part in the rotation, the « superfluid part » staying at rest.

In ref. [6] it was noted that the mathematical methods developed in constructing the superconductivity theory are very general. They may be applied to the description of different fermion systems. Based on the fact that the nuclear matter properties are similar to the electronic structure of metals, in ref. [6] the problem of nuclear matter superfluidity was considered. A. Bohr, B. Mottelson, P. Pines, V. G. Soloviev, S. T. Belyaev et al. [7, 8, 9, 10] have applied the mathematical methods developed in the superfluidity and superconductivity theory to investigate nuclear structure. They have shown that the superconducting pairing correlations are of great importance in medium and heavy nuclei.

Now we shall describe the methods of the superfluid model and the main results obtained by V. G. Soloviev and his colleagues.

Let us consider a system of interacting nucleons with the Hamiltonian

$$H = \sum_{f,f'} \{T(f, f') - \lambda\delta_{ff'}\}\, a_f^+ a_{f'} - \frac{1}{4} \sum_{f_1 f_2 f_2' f_1'} G(f_1, f_2; f_2', f_1')\, a_{f_1}^+ a_{f_2}^+ a_{f_2'} a_{f_1'}\,. \tag{3}$$

Here $a_{f_1}$, $a_f^+$ are the nucleon creation and destruction operators, $f$ is the set of quantum numbers describing the nucleon state, and $\lambda$ stands for the chemical potential.

We perform a linear canonical transformation of the Fermi-operators

(4) $$a_f = \sum_\nu \{u_{f\nu}\alpha_\nu + v_{f\nu}\alpha_\nu^+\}.$$

In order that it does not violate the commutation relations of the operators $\alpha_\nu$ and $\alpha_\nu^+$ the functions $u_{f\nu}$ and $v_{f\nu}$ should satisfy the relations given in ref. [11].

The ground state of the even-even nucleus is defined as a vacuum with respect to the operators $\alpha_\nu$, namely

(5) $$\alpha_\nu|> = 0.$$

Let us introduce the density function $\varrho(f_1, f_2)$ and the correlation function $\Phi(f_1, f_2)$ as follows

(6) $$\varrho(f_1, f_2) = < a_{f_1}^+, a_{f_2} >,$$

$$\Phi(f_1, f_2) = < a_{f_1}, a_{f_2} >.$$

These functions are not independent but linked by the relations of ref. [11].

We find the average value of $H$ over the state (5)

(7) $$< H > = \sum_{f_1 f'} \{T(f_1 f') - \lambda\delta_{ff'}\}\varrho(f_1 f') -$$

$$- \frac{1}{2} \sum_{f_1 f_2 f_2' f_1'} G(f_1, f_2; f_2', f_1')\{\varrho(f_1 f_1')\varrho(f_2 f_2') + \frac{1}{2}\Phi^*(f_1, f_2)\Phi(f_1', f_2')\}.$$

The functions $\Phi$ and $\varrho$ are determined from the minimum condition $< H > = \min$. As a result, we obtain the equations which we write symbolically as follows

(8) $$u(f_1, f_2|\varrho, \Phi) = 0$$

$$\beta(f_1, f_2|\varrho, \Phi) = 0.$$

The chemical potential $\lambda$ is determined from the law of conservation, on the average, of the number of particles

(9) $$N = \sum_f < a_f^+ a_f > = \sum_f \varrho(f, f).$$

The variational principle mentioned is a generalization of the well-know Hartree-Fock method. Among the solutions obtained by this principle there are always solutions of the Hartree-Fock type. Nuclear forces are such that the energy minimum is among the solutions obtained by

the generalized variational principle taking into account nucleon pairing correlations. Therefore the application of this principle in nuclear theory is so efficient.

According to the Bloch-Messiah theorem [12] there exists a linear unitary transformation which transform the function $\Phi(f_1, f_2)$ to the canonical form

$$\Phi(f_1, f_2) = \Phi(f_1)\delta_{f_1, -f_2}\,. \tag{10}$$

It is not difficult to show that in this case the function $\varrho(f_1, f_2)$ is diagonal, i.e.

$$\varrho(f_1, f_2) = \varrho(f_1)\delta_{f_1, f_2}\,. \tag{10'}$$

From the two-particle potential describing the interactions between nucleons, the average nuclear field and the nucleon pair interactions in the states which are conjugate under time reversal, have been separated. The procedure mentioned may be considered as one of the steps of foundation of the independent particle model. The separation of the average field is associated neither with the magnitude nor the form of the potential describing the nucleon interaction. It is clear that the method used above is only an approximate one.

Furthermore, in nuclear theory it is postulated that the average nuclear field corresponds to such a representation when the density matrix $\varrho(f_1, f_2)$ is diagonal for the ground states of several even-even nuclei. In this representation the residual forces reduce completely to the interactions leading to superconducting pairing correlations. Therefore, the ground state may be treated without taking into account the interactions between quasiparticles. This representation is such that for a number of the excited matrix states, $\varrho$ and $\Phi$ are also diagonal.

These statements underly the mathematical apparatus which allows to take into account the pairing superconducting correlations.

According to the superfluid nuclear model the ground state of an even-even nucleus is free of quasiparticles, the excited states are two-quasiparticle, four-quasiparticle ans so on. The ground state and a number of the excited states of odd nuclei are one-quasiparticle states, then follow three-quasiparticle states etc.

Since the forces leading to nucleon pairing correlations are short-range they may be roughly represented in the form of a $\delta$-function. In this approximation they are constant in momentum space. Therefore the matrix elements of these forces over the wave eigenfunctions of the ave-

rage field potential may be assumed to be approximately constant. That is $G(q+, q-; q'-, q'+)$ is independent of $q$ and $q'$

$$G(q+, q-; q'-, q'+) = \frac{\text{Const}}{A} \equiv G\,. \tag{11}$$

Two constants are used, one of them $G_N$ for the neutron system the other $G_Z$ for the proton one. The approximation (11) is rather good. In ref. [13] it is shown that the same values of $G_Z A$ and $G_N A$ well describe pairing energies in a wide region of nuclei $150 < A < 250$.

The blocking effect is of great importance in nuclear theory. The effect on unpaired particles on the superfluid properties of the system in each state was referred to as a blocking effect.

The interaction between nucleons in atomic nuclei leads to a diffuseness of the Fermi surface. It should be noted that the calculated shape of this diffuseness is well justified by the experimental data obtained from one-nucleon transfer reactions.

By taking into account the superconducting pairing correlations one has been able to explain a large amount of experimental data which went beyond the framework of the earlier applied models. So, one has succeeded in explaining not only the appearance of the gap in the spectra of even-even nuclei and the absence of it in odd-odd and odd-mass nuclei but also in giving a qualitative description of the energies of two-quasi-particle excited states. The energies of two-quasi-particle states in even-even nuclei calculated by V. G. Soloviev and his colleagues [14] in 1960-63 describe suprisingly well new experimental data. It is show that the pairing correlations strongly affect the alpha, beta and gamma transition probabilities.

The basic statements of the superfluid nuclear model indicate that for a correct choice of the average field parameters which correspond to the representation when the density matrix is diagonal, there is a reliable theoretical basis for the calculation of the equilibrium deformations of atomic nuclei. This makes it possible to predict the existence of new deformation regions for $50 < N$, $Z < 82$ and $28 < Z < 50$, $50 < N < 82$, as well as the possible existence of a region of long-lived elements for $Z = 114$ and $N = 184$.

In medium and heavy nuclei there are low-lying excited states of three types: rotational states connected with the rotation of deformed nuclei, quasiparticle, and vibrational states. The important success of the superfluid model is the semi-microscopic description of vibrational states. The basic equations can be obtained by the self-consistent field

method, by means of the Green functions and by the approximate second quantization method.

In ref. [11] a mathematical approach is suggested for considering the excited states associated with small vibrations. These excited states are formed by a coherent interaction of many particles. To describe small vibrations, non-diagonal increments $\delta\varrho(f_1, f_2)$ and $\delta\Phi(f_1, f_2)$ are added to the density matrix and to the correlation function. The interactions between quasiparticles lead to the fact that the wave function of the ground state of an even-even nucleus ceases to be the quasiparticle vacuum. The increments $\delta\varrho(f_1, f_2)$ and $\delta\Phi(f_1, f_2)$ are expressed in terms of the function $\mu(\nu_1\nu_2) = < \alpha_{\nu_1}\alpha_{\nu_2} >$ and $\mu^*(\nu_1\nu_2)$ for which the basic equations are derived. The average number of quasiparticles in the ground state is assumed to be small, therefore one uses the approximation

$$< \alpha^+_{\nu_1}\alpha_{\nu_2} > = 0 .$$

As a result, we obtain the integral equation describing small vibrations in the particle-hole and particle-particle channels with interactions of a very general form. In particular cases one obtain the equations of the finite Fermi system theory [15]. Using the multipole-multipole interactions one arrives at the secular equations as applied to spherical nuclei, e.g. in refs. [16, 17] and to deformed nuclei in ref. [18]. When taking into account also the spin-quadrupole interactions one obtains the secular equations deduced earlier in ref. [19].

In studying the vibrational states the most convenient one is the approximate second quantization method. The wave functions of the one-phonon states are found and the alpha beta and gamma transition probabilities and the direct nuclear reaction cross sections are calculated. The wave functions of the collective nonrotational state are a superposition of two-quasiparticle states. The quasiparticle interactions result in the lowering of the energies of the collective states as compared with the two-quasiparticle ones, the main contribution being made by the particle-hole interactions. The stronger the collectivization of the state, the stronger the lowering of the energy. From the equations of the method of approximate second quantization it is possible to obtain, as particular cases, the equations of the Tamm-Dancoff method, the equations of the extended Hartree-Fock theory and the solutions in the case of the adiabatic approximation.

A particular role is assigned to the excited $0^+$ states. In studying them it seems that mathematical difficulties were concentrated on the $0^+$ states. So, among the $0^+$ states there are spurious states, to exclude which one uses the interactions between quasiparticles. A mathematical

method is used, which identifies a superfluous one-phonon $0^+$ state with the ground one. The excited $0^+$ states have a complex structure, containing components which are due to pairing vibrations, beta vibrations, two-phonon states etc.

The development of the semi-microscopic description of the vibrational states in deformed nuclei [18, 20] on the basis of the method of approximate second quantization are very important.

In such an approach one has explained hitherto unclear facts like the very strong lowering of the energies of octupole states in the isotopes of thorium, uranium and plutonium and the lowering of the energies of gamma vibrational states below beta vibrational ones in the isotopes of disprosium and erbium and so on.

The theory describes correctly the vibrational state energies, electromagnetic transition probabilities including such delicate characteristics of these states like their component composition. The most important results of the semi-microscopic theory of vibrational states are connected with the properties of the interaction symmetry rather than with their explicit form (e.g. with their radial dependence).

The development of the semi-microscopic description of vibrational states is an important step in nuclear theory. It connected the location and the structure of vibrational states with the behaviour of the one-particle average field levels. With the aid of the microscopic approach one has succeeded in describing correctly the change of the transition from nucleus to nucleus.

The next step is the construction of the mathematical apparatus describing the interactions of quasiparticles with phonons in deformed nuclei [21, 22]. In odd nuclei the interactions of quasiparticles with phonons lead to the appearance of admixtures in the one-quasi-particle states, to collective non-rotational states and to the appearance of the complex structure states. The complicated structure of the wave functions is revealed in the increase of the reduced probabilities of $E2$ and $E3$ transitions, in spectroscopic factors in direct one-nucleon transfer reactions, in decoupling parameters etc. The available experimental information points to the importance of the interaction of quasiparticles with phonons in deformed nuclei. With increasing energy, the state structure becomes more complicated.

The main reasons responsible for this complication are the coupling of rotation with internal motion and of the interaction of quasiparticles with phonons.

It should be noted that the calculations performed on the basis of the superfluid nuclear model have greatly stimulated the study of nuclear structure. The explanation of a large amount of experimental information

which went beyond the framework of the earlier models, the quantitative description of many characteristics of deformed nuclei and the prediction of the energies, the structure and the particular features of excitations for almost all the low-lying excited states of deformed nuclei have greatly contributed to the investigation of the structure of deformed nuclei. The results of calculations are a guide for experimentalists in setting experiments and analysing experimental data.

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IGAL TALMI (*)

# The Shell Model and Energies of Nuclei and Atoms.

A most dramatic demonstration of periodicity or shell structure in atoms is offered by the *ionization potentials.* The energy required to remove an electron from the atom shows a very distinct behavior which is reproduced in fig. 1. We see sharp rises before reaching noble gas atoms which have closed electron shells and large drops beyond them. This way, the « Magic Numbers » of shell closure can be easily recognized.

When nuclear shell structure became evident [1], physicists were looking for such clear demonstration of the nuclear magic numbers. In this case, the energies required to remove one proton or one neutron from the nucleus were studied. Some plots of these *separation energies* were published which indeed look like the atomic case. Fig. 2 and fig. 3 show such plots copied from standard textbooks.

So impressed are some nuclear physicists with the analogy between nuclear and atomic energies that it is a common belief that magic nuclei are very tightly bound. One book refers to the

« large binding energy of magic number nuclei » and expects that

« as a given state fills with neutrons, the binding energy of the last netron will increase ... for increasing A. ».

Other textbooks state that

« Nuclei containing a magic number of one kind of nucleon are unusually tightly bound ».

« Anomalously high binding associated with the $Pb^{208}$ closed shells ».

« When a shell is filled, the resulting configuration is particularly stable and has an unusually low energy ».

And again

« Nuclei possessing magic numbers of protons and neutrons are more tightly bound ... ».

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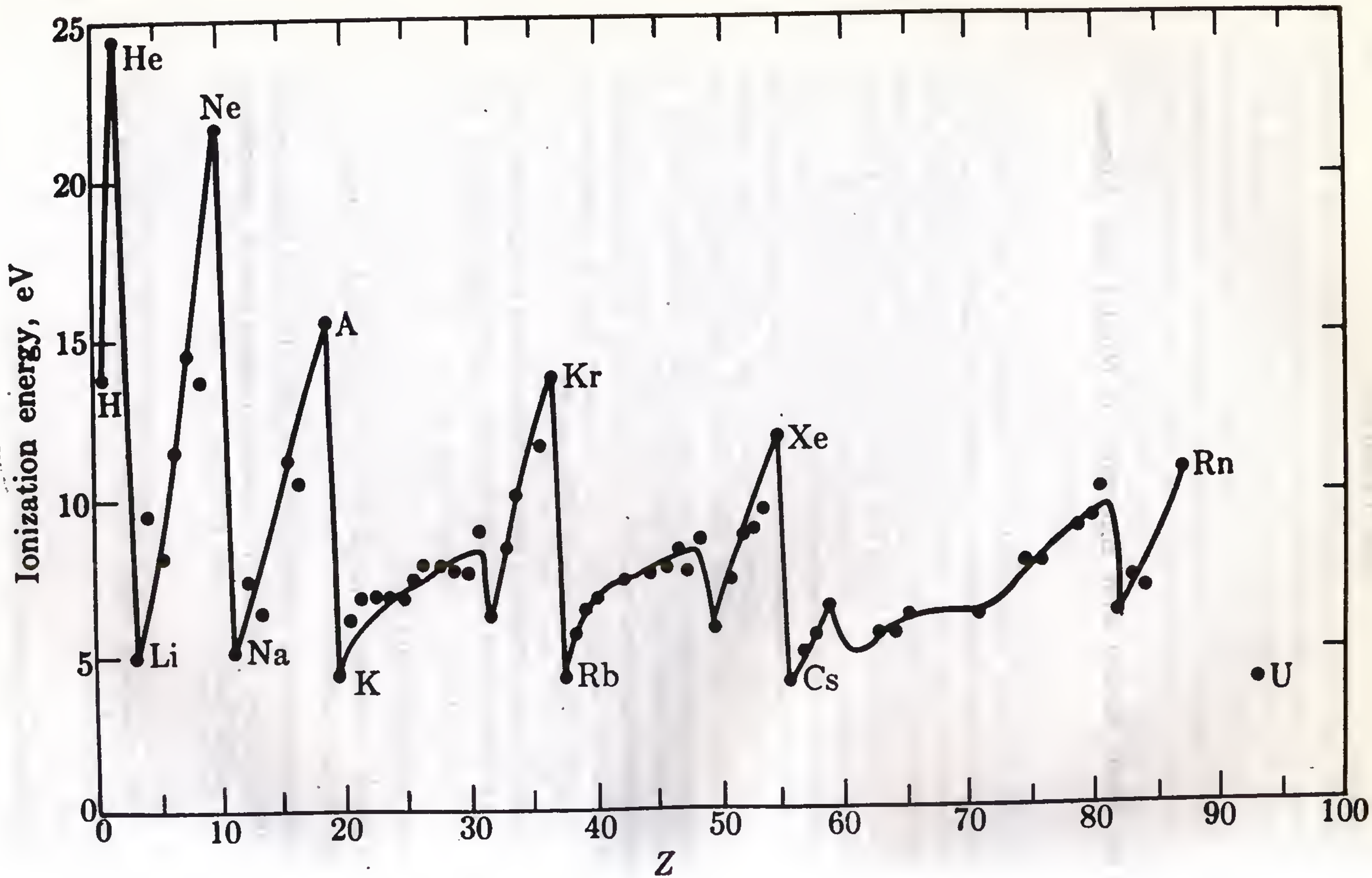


Fig. 1.

Atomic ionization energies.

It is rather difficult to understand what is meant by « large binding energy », « unusually low energy » and « unusually tightly bound ». One possible criterion for tightness could be the binding energy per nucleon.

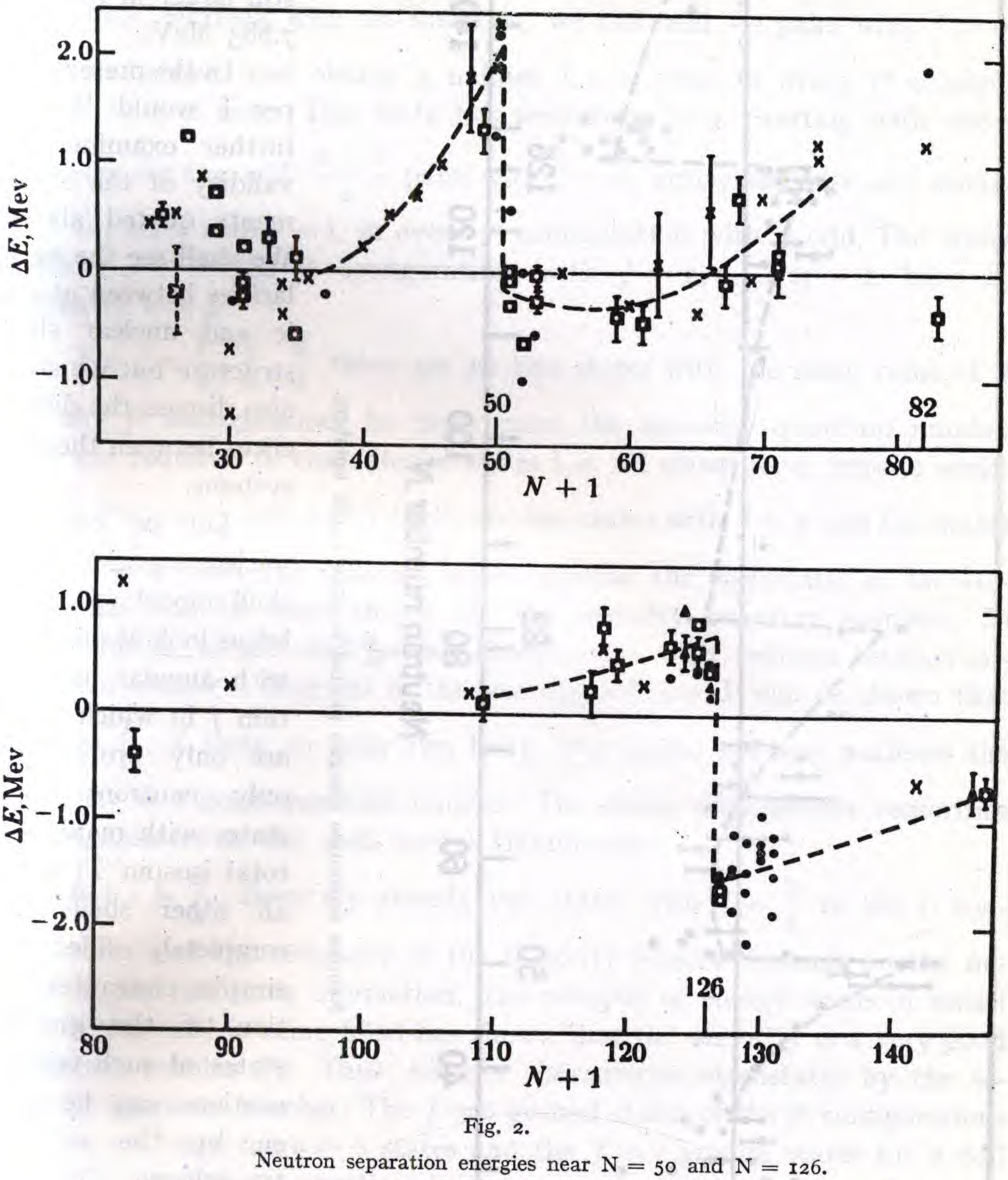


Fig. 2.

Neutron separation energies near N = 50 and N = 126.

Let us examine this quantity [2] in the case of the « anomalously high binding associated with the $Pb^{208}$ closed shells ». We find that the binding energy per nucleon in $Pb^{208}$ is 7.868 MeV which is indeed larger than in $Pb^{210}$ where it is only 7.836 MeV. On the other hand, we find that the binding energy per nucleon in $Pb^{206}$ — 7.875 MeV — is

*larger* than in the doubly magic $Pb^{208}$! If we continue, we find an even larger value in $Pb^{204}$ — 7.880 MeV — and still larger in $Pb^{202}$ — 7.883 MeV.

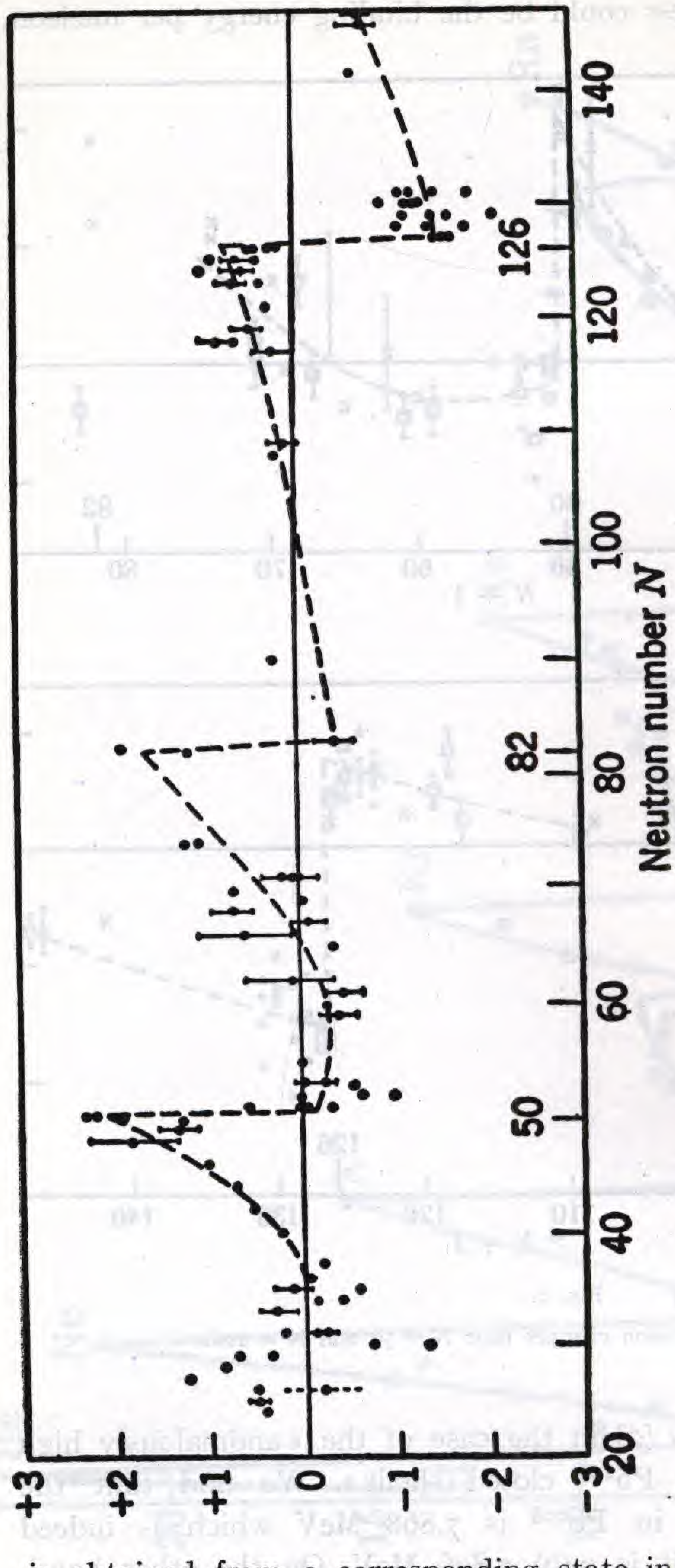


Fig. 3. Neutron separation energies plotted to show magic numbers.

In the present paper I would like to further examine the validity of the statements quoted above. We shall see the similarities between atomic and nuclear shell structure but we shall also discuss the differences between the two systems.

Let us consider nuclear energies in the shell model [3]. First let us look at one shell with angular momentum $j$ in which there are only protons or only neutrons (i. e. states with maximum total isospin $T$) while all other shells are completely filled. A simple characterization of the ground states of such configurations can be given by the seniority scheme. In this scheme, introduced by Racah [4], any state with total spin $J$ in the $j^n$ configuration is obtained from a corresponding state in the smallest configuration $j^v$ with no pairs coupled to $J = 0$, with the same value of $J$, to which

$\frac{n-v}{2}$ nucleon pairs coupled to $J = 0$ are added and the wave function antisymmetrized. The number $v$ is called the seniority of the state. Starting with no nucleons, we can add $\frac{n}{2}$ pairs with $J = 0$, antisymmetrize, and obtain a unique $J = 0$ state in every $j^n$ configuration with $n$ even. This state has seniority $v = 0$. Starting with one $j$ nucleon, we can add $\frac{n-1}{2}$ pairs with $J = 0$, antisymmetrize and obtain a $J = j$ state with $v = 1$, in every $j^n$ configuration with $n$ odd. The states with $J \neq 0$ in the $j^2$ configuration, with $J = 2, 4, \ldots, 2j - 1$, have all seniority $v = 2$.

For $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ there are no two states with the same value of $J$ in any $j^n$ configuration. In these cases the seniority quantum number $v$ is not required to characterize states i. e. all states have definite seniorities. For $j = \frac{7}{2}$ and $n = 4$ there are *two* states with $J = 2$ and *two* states with $J = 4$. Here the question arises whether the eigenstates of the Hamiltonian can be characterized by the seniority quantum numbers. In other words, is the shell model Hamiltonian with residual interactions between nucleons, diagonal in the seniority scheme. It can be shown that for $j = \frac{7}{2}$, if there are only two body interactions between nucleons the seniority is a good quantum number. The states with definite seniorities are eigenstates of the shell model Hamiltonian.

For $j = \frac{9}{2}$, there are already two states with $J = \frac{9}{2}$ in the $j^3$ configuration and the adequacy of the seniority scheme depends on the nature of the two body interaction. The analysis of energy levels of nuclei where this shell is being filled has shown that the seniority is a very good quantum number [5]. Thus, we can characterize eigenstates by the seniority quantum number: The $J = 0$ ground states of the $j^n$ configurations with $n$ even are the $v = 0$ states and the $J = j$ ground states for $n$ odd are the $v = 1$ states mentioned above.

The interaction energies in states of the $j^n$ configuration are linear combinations of those in the $j^2$ configuration. This is true if there are only two body interactions between nucleons and this fact is the basis for the shell model analysis of nuclear energies. However, the interaction energy in the states with lowest seniorities ($v = 0$ and $v = 1$) are linear combinations of only *two* parameters. One is the interaction energy in the $J = 0$

$v = 0$ state and the other is the average interaction energy in the $v = 2$ states with $J = 2, 4, 6, \ldots, 2j - 1$, of the $j^2$ configuration

$$(1) \qquad \overline{V}_2 = \sum_{J>0 \text{ even}} (2J+1) < j^2 J | V | j^2 J > / \sum_{J>0 \text{ even}} (2J+1) .$$

This property is a special case of the fact that the average interaction energy of the states with the same seniority $v$ in the $j^n$ configuration is a linear combination of $V_0 = < j^2 \; J = 0 | V | j^2 \; J = 0 >$ and $\overline{V}_2$ only. There is only one state with $v = 0$, or $v = 1$, in a $j^n$ configuration with $n$ even, or odd, respectively. Thus the interaction energy in such a state is a linear combination of $V_0$ and $\overline{V}_2$.

In order to find the coefficients of $V_0$ and $\overline{V}_2$ we can make use of the seniority operator introduced by Racah [4]

$$(2) \qquad < j^2 JM | q_{12} | j^2 J' M' > = \delta_{JJ'} \delta_{MM'} (2j+1) \delta_{J0} .$$

This is identical with the pairing interaction introduced later in analogy with the B. C. S. theory of superconductivity. It is not a good approximation to the actual nuclear interaction but it is useful for the present calculation. The operator $Q = \sum_{i<k} q_{ik}$ is diagonal in the seniority scheme and its eigenvalues are independent of $J$.

$$(3) \qquad Q(n, v) = \frac{n-v}{2} (2j + 3 - n - v) =$$

$$= - \frac{n(n-1)}{2} + \frac{n-v}{2} (2j+2) + \frac{v(v-1)}{2} .$$

Due to (2) it is clear that the amount of $V_0$ in the average interaction energy in the states with seniority $v$ in the $j^n$ configuration is $Q(n, v) V_0 / (2j+1)$. The total number of two body interactions in such states is $n(n-1)/2$. Thus the average interaction energy is

$$(4) \qquad \frac{Q(n,v)}{2j+1} V_0 + \left( \frac{n(n-1)}{2} - \frac{Q(n,v)}{2j+1} \right) \overline{V}_2 =$$

$$= \frac{n(n-1)}{2} \frac{(2j+2)\overline{V}_2 - V_0}{2j+1} + \frac{n-v}{2} (2j+2) \frac{V_0 - \overline{V}_2}{2j+1} +$$

$$+ \frac{v(v-1)}{2} \frac{(V_0 - \overline{V}_2)}{2j+1} .$$

For states with $v = 0$ or $v = 1$, the last term in (4) vanishes and the second term becomes proportional to $\frac{n}{2}$ if $n$ is even and to $\frac{n-1}{2}$ if $n$ is odd. This is a pairing term which can be written as proportional to the step function $\left[\frac{n}{2}\right]$.

The binding energy which is the total energy of the ground state is the sum of the energy due to the closed shells, the single particle energies of the $j$ nucleons and the interaction energy (4). We can write it as

$$\text{(5)} \qquad \text{B.E.}\,(j^n) = \text{B.E.}\,(n = 0) + nC + \frac{n(n-1)}{2}\alpha + \left[\frac{n}{2}\right]\beta$$

where $C$ is the sum of the kinetic energy of a $j$ nucleon and its interaction energy with the nucleons in closed shells. This is equivalent to the energy of a nucleon in a spherical potential well and is the same in all states of the $j^n$ configuration. The coefficients of the quadratic term and the pairing term are given by (4) as

$$\text{(6)} \qquad \alpha = \frac{2(j+1)\overline{V}_2 - V_0}{2j+1} \qquad \beta = \frac{2(j+1)}{2j+1}(V_0 - \overline{V}_2)\,.$$

In spite of its simplicity, expression (5) is not an empirical relation. It is an exact result and is true for any interaction, central or non-central, local or non-local. The simplicity of this expression is due to the structure of wave functions in the seniority scheme. The different physical theories affect only the values of the coefficients $\alpha$ and $\beta$.

Let us now see what we can learn from the experiment about these coefficients [6]. We can try to see whether we can fit binding energies of nuclei in which a $j$ shell is being filled with constant coefficients $C$, $\alpha$ and $\beta$. This would mean that the two body matrix elements $V_0$ and $\overline{V}_2$ do not change much when going from one nucleus to the next. Actually, a change in B.E. $(n = 0)$ which is linear in $n$ can be absorbed into $C$ and a quadratic change as well as a linear change in $C$ give rise to a modified $\alpha$. The results of such a fit are given in Table I. It deals with the neutron $1f_{7/2}$ shell in nuclei from $Ca^{40}$ to $Ca^{48}$. The other half of the table gives the results for the proton $1f_{7/2}$ shell while the closed shells are those of $Ca^{48}$. The agreement is rather good which gives some confidence in the shell model description of these nuclei.

The coefficient $\beta$ determined by this fit is large and attractive. It is $3.23 \pm 0.20$ MeV for the neutrons and $3.15 \pm 0.13$ MeV for the $1f_{7/2}$ protons. In all other cases we find the same feature — a large and attrac-

TABLE I.

*Binding Energies in Proton and Neutron $1f^n_{7/2}$ Configurations in MeV. The binding energy of $Ca^{40}$ was subtracted from the binding energies of the Ca isotopes. The binding energy of $Ca^{48}$ was subtracted from the binding energies of nuclei with proton configurations.*

| Nucleus | Binding Energy | | Nucleus | Binding Energy | |
|---|---|---|---|---|---|
| | Experimental | Calculated | | Experimental | Calculated |
| ${}_{20}Ca^{41}_{21}$ | 8.36 | 8.42 | ${}_{21}Sc^{49}_{28}$ | 9.62 | 9.69 |
| ${}_{20}Ca^{42}_{22}$ | 19.83 | 19.84 | ${}_{22}Ti^{50}_{28}$ | 21.78 | 21.75 |
| ${}_{20}Ca^{43}_{23}$ | 27.76 | 27.81 | ${}_{23}V^{51}_{28}$ | 29.83 | 29.86 |
| ${}_{20}Ca^{44}_{24}$ | 38.90 | 38.79 | ${}_{24}Cr^{52}_{28}$ | 40.34 | 40.34 |
| ${}_{20}Ca^{45}_{25}$ | 46.32 | 46.31 | ${}_{25}Mn^{53}_{28}$ | 46.91 | 46.88 |
| ${}_{20}Ca^{46}_{26}$ | 56.72 | 56.83 | ${}_{26}Fe^{54}_{28}$ | 55.75 | 55.78 |
| ${}_{20}Ca^{47}_{27}$ | 64.00 | 63.90 | ${}_{27}Co^{55}_{28}$ | 60.81 | 60.74 |
| ${}_{20}Ca^{48}_{28}$ | 73.94 | 73.98 | ${}_{28}Ni^{56}_{28}$ | 68.01 | 68.06 |

tive pairing term. This result is not due to the pairing interaction. It is due to one feature of the nuclear interaction — that the $J = 0$, $v = 0$ state lies considerably below the *center of mass* of the $v = 2$ levels with $J = 2, 4, \ldots, 2j - 1$.

The coefficient $\alpha$ in the quadratic term turns out to be smaller than $\beta$ but it has always the opposite sign and it is *repulsive* [6]. It is $-0.23 \pm \pm 0.01$ MeV for the $1f_{7/2}$ neutrons and $-0.79 \pm 0.01$ for the protons (here it includes also the Coulomb repulsion). This repulsion is a direct consequence of the properties of the effective nuclear interaction. It follows from the *saturation* of nuclear energies and from the existence of a strong *symmetry energy* as we shall presently see.

If there are both protons and neutrons in the $j$ orbit, the eigenstates of a charge-independent Hamiltonian are characterized by the symmetry of the wave functions with respect to the spatial coordinates and spins. This symmetry is uniquely determined by the value of the total isospin $T$. The seniority scheme is not a very good approximation if $T < \frac{n}{2}$. However, it can still provide a simple picture in which the important aspects of the nuclear interaction are clearly exhibited. In addition to the seniority $v$, also the isospin of the state in the minimal $j^v$ configuration should now be specified. It is called the reduced isospin $t$. The $J = 0$, $v = 0$ state has $t = 0$ irrespective of the total isospin $T$. The $J = j$,

$v = 1$ state has $t = \frac{1}{2}$ with $T = \frac{1}{2}, \frac{3}{2}, \ldots, \frac{n}{2}$. The $J = 2, 4, 6, \ldots,$ $2j - 1$ states of the $j^2$ configuration with $v = 2$ have $t = T = 1$ while those with odd values of $J$ ($J = 1, 3, \ldots, 2j + 1$) have also $v = 2$ but for them $t = T = 0$.

In analogy with (4) and (5), the interaction energies of states with lowest seniorities in even-even and odd-even nuclei are linear combinations of only three parameters. Two of these are $V_0$ and $\overline{V}_2$ and the third ($\overline{V}_1$) is the average interaction energy of the states with odd $J$ in the $j^2$ configuration. The interaction energy in ground states is given by

$$\frac{n(n-1)}{2}\alpha + \left[\frac{n}{2}\right]\beta + \left\{T(T+1) - \frac{3}{4}n\right\}\gamma \tag{7}$$

TABLE II.

*Binding Energies in* $1d^n_{3/2}$ *Configurations in MeV.*
*The binding energy of* $S^{32}$ *was subtracted from all binding energies.*

| Nucleus | Binding Energy | |
|---|---|---|
| | Experimental | Calculated |
| ${}_{16}S^{33}_{17}$ | 8.64 | 8.68 |
| ${}_{16}S^{34}_{18}$ | 20.06 | 20.07 |
| ${}_{16}S^{35}_{19}$ | 27.05 | 27.13 |
| ${}_{16}S^{36}_{20}$ | 36.93 | 36.89 |
| ${}_{17}Cl^{33}_{16}$ | 2.29 | 2.33 |
| ${}_{17}Cl^{34}_{17}$ | 13.79 | 13.72 |
| ${}_{17}Cl^{35}_{18}$ | 26.43 | 26.29 |
| ${}_{17}Cl^{36}_{19}$ | 35.01 | 35.08 |
| ${}_{17}Cl^{37}_{20}$ | 45.33 | 45.17 |
| ${}_{18}Ar^{35}_{17}$ | 19.67 | 19.51 |
| ${}_{18}Ar^{36}_{18}$ | 34.94 | 34.79 |
| ${}_{18}Ar^{37}_{19}$ | 43.73 | 43.90 |
| ${}_{18}Ar^{38}_{20}$ | 55.57 | 55.71 |
| ${}_{19}K^{37}_{18}$ | 36.81 | 37.03 |
| ${}_{19}K^{38}_{19}$ | 48.72 | 48.85 |
| ${}_{19}K^{39}_{20}$ | 61.94 | 61.84 |
| ${}_{20}Ca^{39}_{19}$ | 54.64 | 54.54 |
| ${}_{20}Ca^{40}_{20}$ | 70.28 | 70.25 |

where $\alpha$, $\beta$ and $\gamma$ are linear combinations of $V_0$, $\overline{V}_2$ and $\overline{V}_1$. There are not many cases in which a mass formula based on (7) can be compared with experiment. It gives good results in the $1d_{3/2}$ shell as shown in Table II, and fair results in the $1f_{7/2}$ shell (with both protons and neutrons [7]).

It is significant that in all cases considered, the coefficient of the quadratic term is rather small ($\alpha = 0.11 \pm 0.04$ MeV for the $1d_{3/2}$ shell).

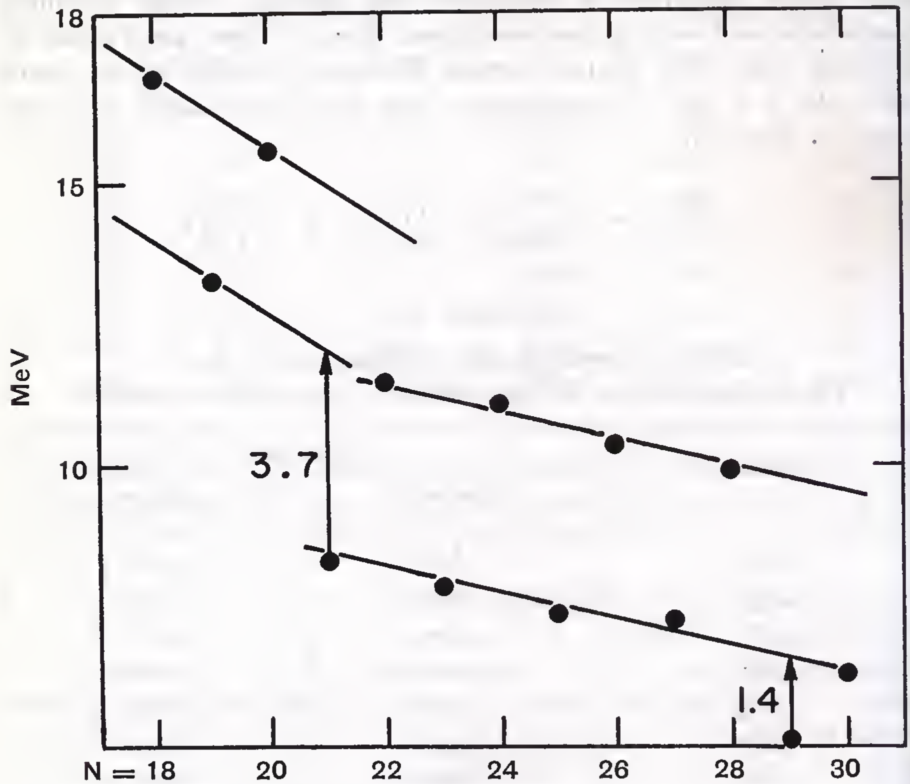


Fig. 4.
Neutron separation energies of calcium Isotopes (Z = 20).

This means that saturation is very well obeyed *within each shell.* The pairing term is large and attractive as in (5). The interesting new term is the last one which exhibits the symmetry energy. Its coefficient is rather large and *repulsive* (it is $-1.84 \pm 0.08$ MeV in the $1d_{3/2}$ shell) so that the lower the value of $T$ (and the higher the space and spin symmetry), the lower the energy. This is a well known fact and so should be its consequences.

If we have only protons or neutrons outside closed shells, i.e., if $T = \frac{n}{2}$,

we see that the symmetry energy in (7) contributes to the quadratic term. The coefficient of $n(n-1)/2$ becomes in this case $\alpha + \frac{\gamma}{2}$. Thus, a large

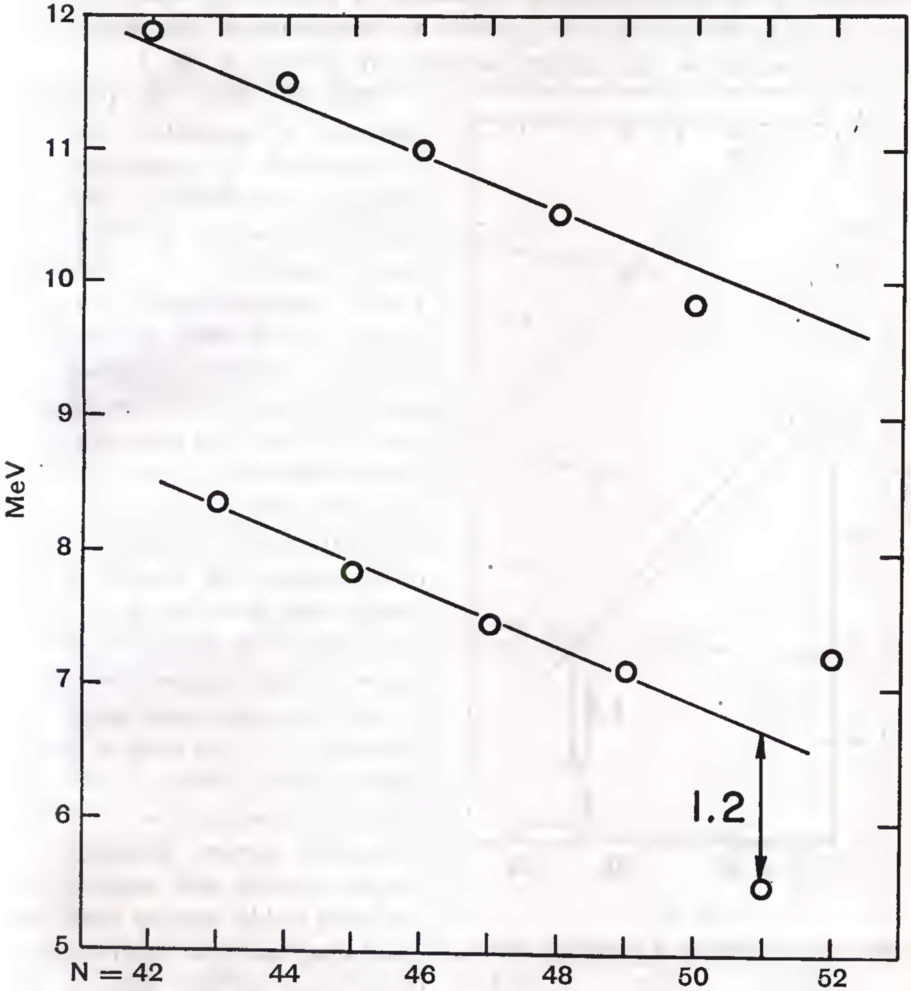


Fig. 5.

Neutron separation energies of krypton Isotopes (Z = 36).

attractive symmetry term gives rise to a repulsive quadratic term in the interaction energy of identical nucleons.

Let us now come back to the expression of the binding energy and see what it implies for separation energies. Since (5) is quadratic, the differences between neighboring nuclei are linear in $n$. Due to the pairing

term, the separation energies should lie on two parallel straight lines. The upper line corresponds to even values and the lower to odd values of $n$. The distance between the two lines along the y-axis is equal to the coefficient of the pairing term $\beta$. The slope of the lines is equal to $\alpha$ and since it is repulsive both lines go down for increasing $\bar{n}$. The neutron separation energies in the calcium isotopes are plotted in fig. 4.

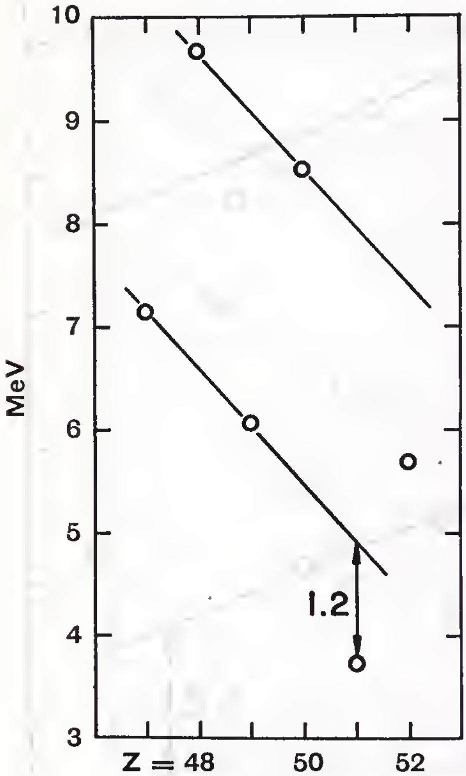


Fig. 6.
Proton separation energies of nuclei with N = 64.

We see that the predicted behavior of separation energies is borne out by experiment. In particular we realize that the separation energies *go down* as a magic number is approached! Thus, a magic nucleus is *not* more tightly bound than its *preceding* even-even neighbors. This is the case in all regions of the periodic table as should be expected from the saturation properties of the nuclear interaction. If this is indeed so, what makes a magic nucleus really magic? The answer can be simply seen from fig. 4. It is the *large drop* of the separation energy *beyond* a magic number that makes a magic nucleus more *stable* and abundant [6]. This drop is due to higher kinetic energy in the new orbit and possibly also to smaller interaction energy. Stability is a relative quality and magic nuclei are more stable because nuclei beyond them are *less* tightly bound. Other cases of this behavior are shown in fig. 5 (for the krypton isotopes $Z = 36$), fig. 6 (Nuclei with $N = 64$) exhibiting the magic number 50 for neutrons and protons respectively and fig. 7 (for the lead isotopes, $Z = 82$), with the magic number $N = 126$. The deviations from the straight lines of fig. 7 before 126 are due to the occurance of a $p_{1/2}$ orbit at the end of the shell. In particular, the pairing energy in this orbit is very low.

We can now ask how could separation energies be plotted that showed a definite rise before a magic number. The explanation is very simple. The plots show *differences* of the actual separation energies from an ave-

rage value obtained from some smooth mass formula. The average line goes through the middle of the drop and therefore the differences show a spurious rise before a magic number and a smaller drop beyond it.

Let us now come back to ionization energies of atoms and discuss the cause of the large rise before reaching a magic atom. This rise is

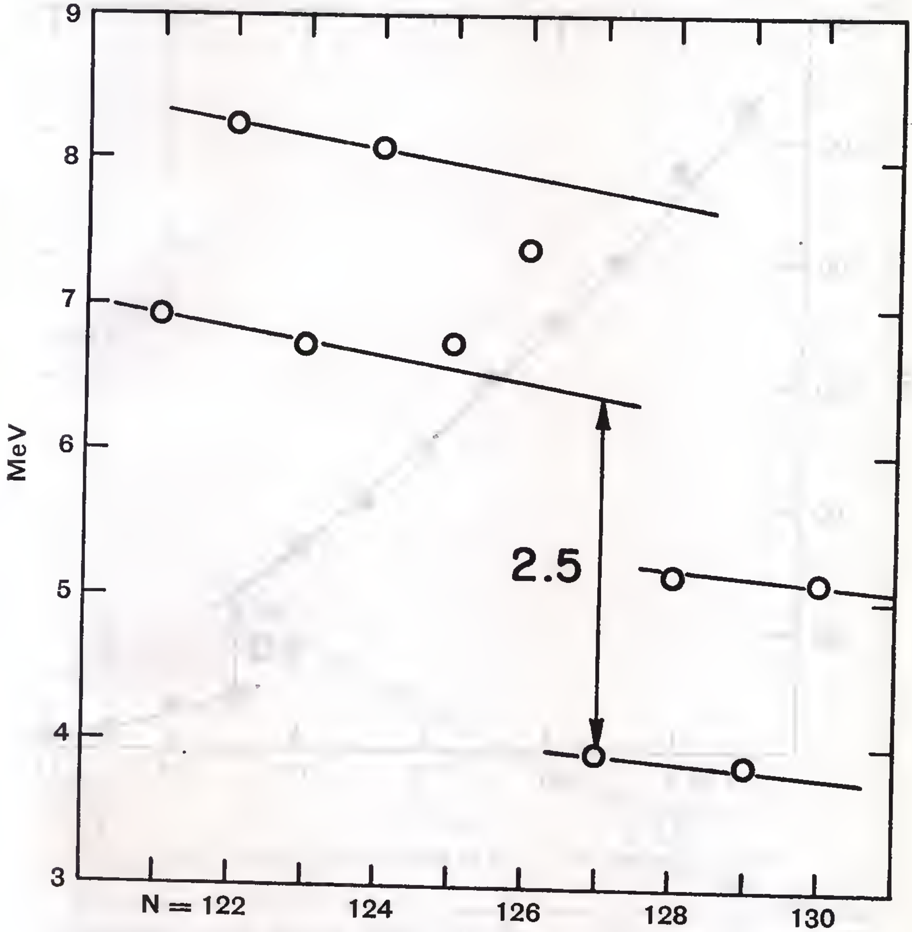


Fig. 7.

Neutron separation energies of lead isotopes.

certainly not due to the mutual interaction of electrons in the shell since this interaction is *repulsive*. This is a trivial fact but it is often ignored by people who look for superficial analogies. The usual plot of ionization energies is made for *neutral* atoms. Thus, when a shell is being filled, the central charge $Z$ increases whereas the additional mutual repulsion is

not so effective. In other words, the « screening » due to electrons in the same orbit is not very efficient. This causes the rise in ionization energy. When an electronic shell is completely filled, the next electron goes into a new orbit with higher kinetic energy and is screened very effectively by the inner electrons, thus making it much less bound.

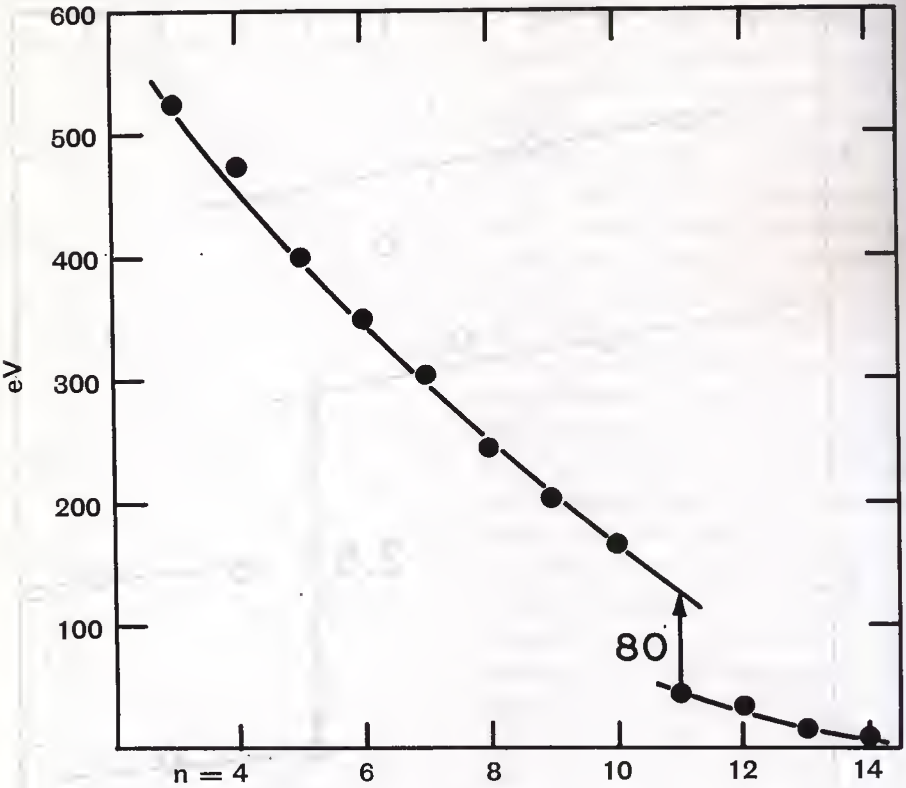


Fig. 8.

Ionization energies for Z = 14 as function of the electon number n.

We saw that apart from the attractive pairing term, the interaction between identical nucleons is repulsive in surprising analogy to the repulsive Coulomb interaction between the electrons. The analog of the attractive atomic central charge is the attraction of the nucleons of the other kind. This is seen in (7) but we find also an attraction between protons and neutrons in different orbits. This attraction between protons and neutrons is the source of the attractive central field of the nuclear shell model. Thus, if we look at the change in separation energies of one kind of identical nucleons, we can increase the attractive field by a ju-

dicious addition of nucleons of the other kind. This way we can obtain even a rise in separation energies. If we go roughly along the stability line of nuclei, there is no significant increase of the separation energies as a magic number is approached.

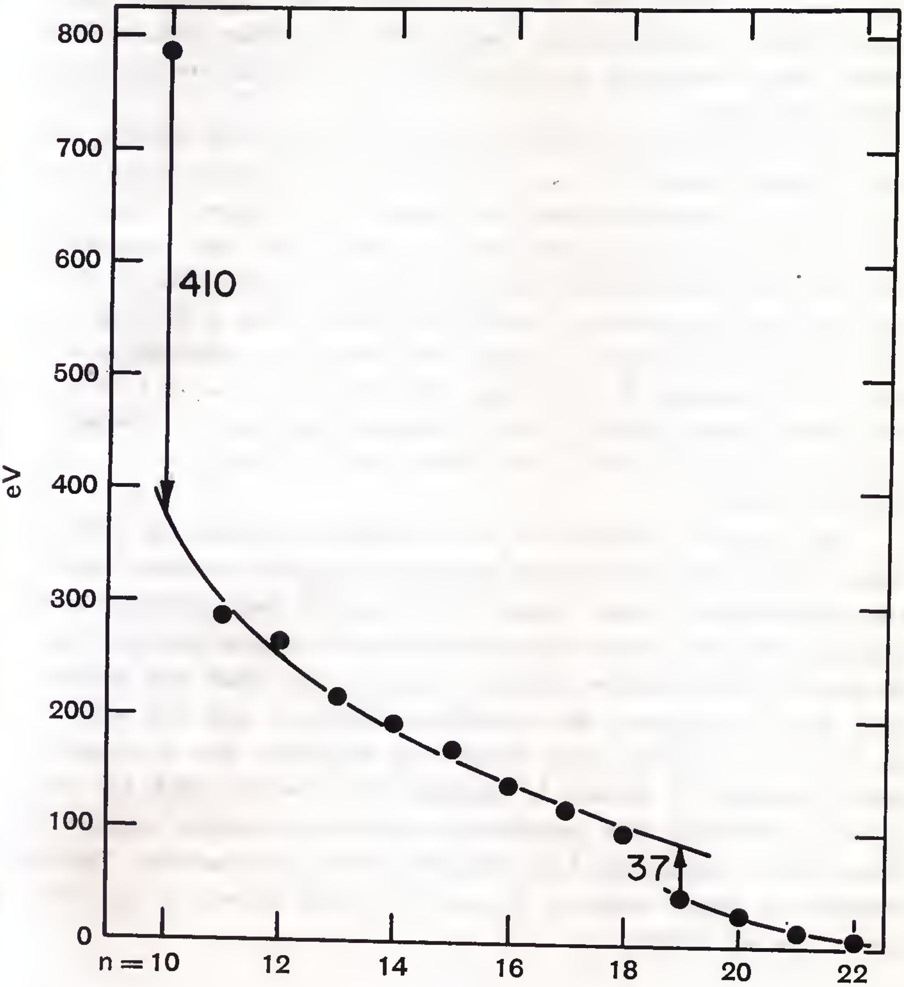


Fig. 9.
Ionization energies for Z = 22 as function of the electon number n.

As the analogy between nuclei and atoms is now clearly defined, we can look again at atomic ionization energies. We can look at the change in ionization energies as the number of electrons is increased while the central attractive field remains unchanged. This involves ionization potentials of ions as well as of neutral atoms [8]. Due to the repulsion

between electrons we expect the ionization energy, for fixed $Z$, to go down as the number of electrons is increased. We expect to see shell closures by a bigger drop in ionization energy. No pairing effects should be expected since the electrostatic interaction between electrons is completely repulsive, unlike the attractive pairing term in nuclei. Thus, the lowest states of an electronic configuration are those with highest seniority and consequently have no pairing. As a result, no odd even variation will appear.

As an example, we see in fig. 8 ionization energies of the various ions with a central charge $Z = 14$. As the number of electrons $n$ is increased, the ionization energies decrease but beyond $n = 10$ there is a much larger drop. This clearly demonstrates the closure of the shell containing the first and second $s$-orbits and the first $p$-orbit. The drop beyond $n = 10$ is clearly seen also in fig. 9 where the nuclear charge is $Z = 22$. Due to the increase in the central charge, the ionization energy for $n = 10$ is now 788 eV instead of 167 eV and the drop from $n = 10$ to $n = 11$ is also several times bigger. In fig. 9 the large drop beyond $n = 19$ is also evident, where the closed shells include also the third $s$-orbit and the second $p$-orbit.

We see that in spite of the large differences between the interactions which govern the atomic and nuclear many-body systems, there are clear similarities between them. The repulsive term between identical nucleons gives rise to the analogy with the electrostatic repulsion between electrons. The attractive pairing term does not upset the analogy, its only effect is to cause the separation energies of odd and even nuclei to be on two parallel lines instead of the single line of atomic ionization energies. It should be pointed out, however, that the analogy is only qualitative. The saturation properties of nuclear energies make them behave differently from the electrostatic interactions. The manifestation of magic numbers in nuclei as well known, is far less dramatic than in atoms.

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J. P. ELLIOTT (*)

# The Classification of Shell-Model States.

It is a remarkable fact that, although the nuclear forces between nucleons (neutrons and protons) are so very different from the atomic (Coulomb) forces between electrons, nevertheless the properties of nuclei are dominated by a shell structure similar to that underlying the Mendeleev periodic system. The differences between the two systems are illustrated below,

| | *Atom* | *Nucleus* |
|---|---|---|
| | Attracting central nucleus | No attracting centre |
| Inter-particle forces | Repulsive | Attractive |
| | Largely spin-independent | Strong spin-dependence |
| | Long range $1/r$ | Short range $e^{-\mu r}/r$ ($\mu \sim 0.7 \times \times 10^{13}$ cm$^{-1}$) |
| | Largely Central forces | Strong non-Central forces (both Tensor and Spin-Orbit). |

The atomic shell structure is perhaps to be expected because of the strong nuclear attraction. In the nucleus, the shell structure results from the rather complicated saturation characteristics of nuclear forces. The saturation is caused by three distinct features

(1) The repulsive core in nuclear forces at distances less than about 0.5 $(10)^{-13}$ cm.

(2) The exchange properties of nuclear forces which give a net repulsion in odd states of relative motion.

(3) The strong tensor force, without which the neutron and proton would not bind together but which, in a closed shell, contributes nothing in first order.

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In both fields therefore one has the problem of the zero-order degeneracy in an unfilled shell of $n$ particles. In atoms they will be $l$-shells ($l^n$) but in nuclei, except for the lighter ones, the two-body spin orbit force, which has the form

$$\{(\sigma_1 + \sigma_2) \cdot (r_{12} \wedge p_{12})\} f(r_{12}) \, ,$$

generates a strong one-body spin-orbit force in the average field which gives periodicities according to the filling of $j$-shells ($j^n$). It is true that there will be substantial mixing of configurations but, unless two configurations lie particularly close, this may be incorporated by using an «effective interaction». The effective interaction may be treated empirically, as in the work of Racah [1] (atoms) and Talmi [2] (nuclei), by treating each Slater integral as an adjustable parameter in a least squares fit. On a more fundamental basis one may calculate the effective interaction from the true interaction by using perturbation theory. In nuclei, the strong repulsive core demands a modification of perturbation theory using the reaction matrix method of Brueckner.

The main part of this talk will be concerned with a pure configuration $l^n$ (or $j^n$) or perhaps the mixing of two or three configurations. In principle, the energy levels of the system are found simply by diagonalising the matrix of the two-body force in some arbitrary complete set $\psi_1$ of wave functions of the configuration $l^n$ (or $j^n$). In practice, especially in nuclei, the size of such matrices can be prohibitively large and the calculation of matrix elements very laborious. One therefore studies possible bases for the complete set with the hope of finding a basis which is either simple or provides a good approximation to the eigen-functions of the energy matrix or, ideally, achieves both aims.

The mathematical tool with which one studies this problem is Group Theory and it was G. Racah [3] who first showed how it could be used. Consider first an atomic $l$-shell. Including spin, there are $(4l + 2)$ substates of a single particle and Racah studied the most general unitary transformations in this space. They form the group $U_{4l+2}$ whose generators may conveniently be taken as the tensor products

$$(a^+ a)^{(rk)}_{pq}$$

where the creation operator $a^+$ is a tensor of degree $1/2$ in spin space and degree $l$ in orbital space. The degrees of the tensor product in the two spaces are denoted by $r$ and $k$ with components $p$ and $q$. Thus $r = 0$ or

1 and $k = 0, 1, 2, \ldots, 2l$. The allowed antisymmetric states of $l^n$ then belong to the same irreducible representation

$$\underbrace{[1\ 1 \ldots 1]}_{n}$$

of this group. Racah began the study of sub-groups of $U_{4l+2}$ and pointed out the general chain

$$(1) \qquad \begin{array}{ccccccc} U_{4l+2} & \rightarrow & SU_2 \times U_{2l+1} & \rightarrow & SU_2 \times R_{2l+1} & \rightarrow & SU_2 \times R_3 \\ (a^+a)^{rk} & & (a^+a)^{10}\ (a^+a)^{0k} & & (a^+a)^{0k(odd)} & & (a^+a)^{01} \end{array}$$

with the generators indicated below each new group. The generators of $SU_2$ and $R_3$ are just the spin and orbital angular momenta. The wave functions may then be classified by the representation labels of the groups in the chain

$$(2) \qquad | S(\sigma_1\, \sigma_2 \ldots \sigma_l) L > .$$

It is unnecessary to include a label for the group $U_{2l+1}$ since it is determined by the value of $S$. It would be $[22 \ldots 211 \ldots 1]$, where the symbol 2 occurs $\frac{n}{2} - S$ times and the symbol 1 occurs $2S$ times. Here $\sigma_i = 2$, 1 or 0 and $\sigma_i \geq \sigma_{i+1}$.

The classification (2) is not complete. In other words, there occur several independent states with the same values of the labels in (2). Racah searched for further groups to include in the chain but found such a group only in particular cases. For example, in the $f$-shell the group $G_2$, generated by the operators $(a^+a)^1$ and $(a^+a)^5$, lies between $R_7$ and $R_3$. Even this additional label does not lead to a complete classification in the $f$-shell.

Further insight into the structure of the $l^n$ shell was reached by enlarging [4] the group beyond $U_{4l+2}$ and then taking an alternative path to $SU_2 \times R_{2l+1}$ bypassing $U_{4l+2}$. The larger group is $R_{8l+4}$ with generators $(a^+a^+)^{rk}$ and $(aa)^{rk}$ in addition to those of $U_{4l+2}$. The alternative path is

$$(3) \qquad \begin{array}{ccccc} R_{8l+4} & \rightarrow & SU_2 \times Sp_{4l+2} & \rightarrow & SU_2 \times SU_2 \times R_{2l+1} \\ & & (a^+a)^{rk} & & a^+a)^{10}\ (a^+a)^{0k(odd)} \end{array}$$

with $(r + k)$ odd, which contains the new «quasi-spin» group $SU_2$ with generators $(a^+a)^{00}\ (a^+a^+)^{00}\ (a\ a)^{00}$. Thus we have an extra quasi-spin label $Q$ but it may be shown that this is closely related to the seniority by the

relation $Q = l + \frac{1}{2} - \frac{1}{2} v$. The three operators of the quasi-spin group have simple interpretations viz, the number operator and the pair creation and destruction operators. It is natural to choose the number operator to be diagonal on the 'magnetic' sub-states. Thus a quasi-spin multiplet runs over states with different numbers of particles. For illustration, the atomic $d$-shell is classified in table 1, in which the possible combinations $S(\sigma_1\sigma_2)$ are entered for each value of $n$ and $v$. Notice how the states with seniority $v = 0$ form a quasi-spin sextet, those with seniority $v = 1$ form a quintet and so on.

The introduction of Racah's group chain leads to a simple and elegant technique for calculating matrix elements making use of the simple algebra of the group operators. But does the classification have physical significance? The essence of the group $R_{2l+1}$ is that, in the two body system, it distinguishes the $^1S$ state from the other singlets and does not separate the triplet states. In practice the two electron spectra certainly have the $^1S$ state higher than the other states which are however considerably spread. Consequently the states classified according to $R_{2l+1}$ are considerably mixed by the Coulomb interactions. One could perhaps argue that the low states tend to have as few pairs coupled to $^1S$ as possible. In other words they have high 'seniority' $v$, where $v$ is the number of unpaired particles and in the notation of (2), $v = 2(S + b)$ where $b$ is the number of times that the symbol 2 occurs in $(\sigma_1, \sigma_2, \ldots, \sigma_l)$.

We see how this deeper insight into the shell structure has been brought about by extending to groups which violate the conservation of particle number. However, the quasi-spin group has generators which only change the particle number by two and one may ask if it is possible to generalise further. In fact the most general unitary group would be $U_{2^{4l+2}}$ since $2^{4l+2}$ is the total number of states in the entire shell. The generators would transform from any state to any other, even from the empty to the full shell, involving the maximum possible change in particle number. One can then look for sub-groups of $U_{2^{4l+2}}$. Moshinsky [5] has begun to explore this region.

Very recently, Armstrong and Judd [6] have introduced yet another chain of groups which gives a more complete classification in a very simple way. More importantly, it seems that the calculation of matrix elements will be greatly simplified and the use of fractional parentage coefficients is avoided. It has the disadvantages that the particle number is not diagonal and that one must work separately with the spin-up and the spin-

TABLE I.

*Classification of the atomic d-shell. The possible values of $S(\sigma_1\sigma_2)$ are entered for each seniority v and number n. The reduction from $(\sigma_1\sigma_2)$ to L is given below the table.*

| $n \backslash v$ | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | 0 (00) | | | | | |
| 1 | 0 (00) | $\frac{1}{2}$ (10) | | | | |
| 2 | | | 0 (20)<br>1 (11) | | | |
| 3 | | $\frac{1}{2}$ (10) | | $\frac{1}{2}$ (21)<br>$\frac{1}{2}$ (11) | | |
| 4 | 0 (00) | | 0 (20)<br>1 (11) | | 0 (22)<br>1 (21)<br>2 (10) | |
| 5 | | $\frac{1}{2}$ (10) | | $\frac{1}{2}$ (21)<br>$\frac{3}{2}$ (11) | | $\frac{1}{2}$ (22)<br>$\frac{3}{2}$ (11)<br>$\frac{5}{2}$ (00) |
| 6 | 0 (00) | | 0 (20)<br>1 (11) | | 0 (22)<br>1 (21)<br>2 (10) | |
| 7 | | $\frac{1}{2}$ (10) | | $\frac{1}{2}$ (21)<br>$\frac{3}{2}$ (11) | | |
| 8 | 0 (00) | | 1 (20)<br>1 (11) | | | |
| 9 | | $\frac{1}{2}$ (10) | | | | |
| 10 | 0 (00) | | | | | |

The *L*-values are (00) *S*, (10) *D*, (20) *DG*, (11) *PF*, (21) *PDFGH*, (22) *SDFGI*.

down particles. Consider the spin-up space alone, i.e. states of maximum multiplicity. Then the group chain is

$$(4)\qquad \begin{array}{ccccc} R_{4l+2} & \rightarrow & R^{\lambda}_{2l+1} \times R^{\mu}_{2l+1} & \rightarrow R^{\lambda}_{3} \times R^{\mu}_{3} & \rightarrow R_3 \\ (a^+a)^k\,(a^+a^+)^k\,(aa)^k & & (\lambda^+\lambda)^{k(odd)}\,(\mu^+\mu)^{k(odd)} & (\lambda^+\lambda)^1\,(\mu^+\mu)^1 & (a^+a)^1 \end{array}$$

where the new operators $\lambda$ and $\mu$ are defined as

$$(5)\qquad \lambda^+_m = \sqrt{\frac{1}{2}}\,(a^+_m + (-)^{l-m}\,a_{-m}),$$

$$\mu^+_m = \sqrt{\frac{1}{2}}\,(a^+_m - (-)^{l-m}\,a_{-m}).$$

They look like quasi-particle operators but, if $m$ is allowed to run over the full range $-l \leq m \leq l$, they do not satisfy the necessary anti-commutation relations. In particular, $\lambda^+_{-m} = (-)^{l-m}\lambda_m$ and $\mu^+_{-m} = -(-)^{l-m}\mu_m$. However, by restricting the space to positive $m$, the relations are satisfied and we have the concept of independent $\lambda$ and $\mu$ quasi-particles in an *l-dimensional* space, rather than one of $(2l + 1)$ dimensions. One can introduce the concept of angular momentum $l_\lambda$ and $l_\mu$ in each factorised space as the representation labels for $R^{\lambda}_3$ and $R^{\mu}_3$. It follows that the physical total orbital angular momentum operator is given by $L = l_\lambda + l_\mu$. It is further readily shown that only the single representation $\left(\frac{1}{2}\,\frac{1}{2} \cdots \frac{1}{2}\right)$ can occur for both $R^{\lambda}_{2l+1}$ and $R^{\mu}_{2l+1}$. The possible values for $l_\lambda$ and $l_\mu$ may then be deduced and the results are shown in table 2 for $l \leq 6$.

In classifying the states, it is convenient to consider even and odd numbers of particles separately. In each case the states may be denoted by

$$(6)\qquad |\, l_\lambda l_\mu L >$$

being a simple vector-coupling of the $\lambda$ and $\mu$ angular momenta. The two cases are distinguished by the choice of vacuum for the quasi-particles which may be taken as either

$$\prod_{m<0} a^+_m\,|\,0>$$

or

$$\prod_{m\leq 0} a^+_m\,|\,0>.$$

One may readily check that the $L$-values obtained from the vector coupling (6), with the $l$-values taken from table 2, are the same as those of the usual classification. Moreover, for maximum spin, the classification (6)

TABLE II.

*The $l_\lambda$ (or $l_\mu$) values in a factorised classification of the $l^n$ shell.* (*From Armstrong and Judd*).

| $l$ | $l_\lambda$(or $l_\mu$) |
|---|---|
| 1 | $\frac{1}{2}$ |
| 2 | $\frac{3}{2}$ |
| 3 | 0,3 |
| 4 | 2,5 |
| 5 | $\frac{5}{2}, \frac{9}{2}, \frac{15}{2}$ |
| 6 | $\frac{3}{2}, \frac{9}{2}, \frac{11}{2}, \frac{15}{2}, \frac{21}{2}$ |

is complete for $l \leq 8$. For example in the $d$-shell we have $L = 3, 2, 1, 0$ from $(3/2)^2$. This is in agreement with the $L$-values for even $n$, viz. $L = 0$ for $n = 0$, $L = 1, 3$ for $n = 2$ and $L = 2$ for $n = 4$. The same sets of $L$-values occur for odd $n$.

In evaluating matrix elements of two-body operators one may first write the operator in terms of $\lambda$ and $\mu$ operators. Then, making use of the factorisation the matrix element may be expressed in terms of a few simple reduced matrix elements in each space. These are readily deduced and have been tabulated by Armstrong and Judd. There is no need for elaborate tables of fractional parentage coefficients.

I have spoken mostly about an $l^n$ shell but in nuclei one is more often interested in a $j^n$ shell. In fact the classification for $j^n$ follows a path very similar to that for $l^n$. There are small subtle differences. For example in the chain analogous to (1) the group $R_{2j+1}$ is replaced by the symplectic group $Sp_{2j+1}$. The reason for this is simply that the two-particle scalar $L = 0$ of $l^2$ is symmetric while the two-particle scalar $J = 0$ of $j^2$ is antisymmetric.

From a physical point of view the use of seniority is most useful in nuclei with like particles in the shell. Then the short range nuclear force brings the $J = 0$ state of $j^2$ lower in energy and well separated from

other $J$. In this case it is the low seniority $v = 0$, $J = 0$ for even $n$ and $v = 1$, $J = j$ for odd $n$ which lie lowest. This of course is opposite from the atomic situation because the inter-particle forces are now attractive rather than repulsive. With both neutrons and protons present in the shell seniority is still a good quide, but the mixing is much greater.

The method of Armstrong and Judd does not appear to be applicable to a shell $j^n$ of like particles (e.g. all neutrons). However, in practice one is interested in both neutrons and protons in the shell $j^n$ in an iso-spin classification. For this system, the method does extend (see Elliott and Evans [7]) by defining operators

$$\lambda^+_{ms} = \sqrt{\frac{1}{2}}\,(a^+_{ms} + (-)^{j+\frac{1}{2}-m-s}\,a_{-m-s})$$

$$\mu^+_{ms} = \sqrt{\frac{1}{2}}\,(a^+_{ms} - (-)^{j+\frac{1}{2}-m-s}\,a_{-m-s})$$

where $m$ is the magnetic label for $j$ and $s = \pm\frac{1}{2}$, denoting neutron or proton respectively. The essential point for the factorisation is that the phase $(-)^{m+s}$ is unchanged when the signs of both $m$ and $s$ are changed. This is also true of the phase $(-)^m$ in (5) since in that case $m$ is integral. For the half-integral case the phase $(-)^m$ will change with the sign of $m$ preventing the factorisation of $\lambda$ and $\mu$. In fact, for the $j^n$ shell, with iso-spin, the method of Armstrong and Judd seems even more appropriate since one no longer has to separate the spin-up and spin-down spaces. The classification is now

$$|\,J_\lambda T_\lambda,\, J_\mu T_\mu;\, JT > \tag{7}$$

and this covers both even and odd numbers of particles, unlike the $l^n$ shell. As an illustration, table 3 shows the possible values of $J_\lambda$ and $T_\lambda$ for $j \leq 7/2$. There is still the small problem of constructing states with definite number of particles since the set (7), if symmetrized or anti-symmetrised between $\lambda$ and $\mu$, contains mixtures of $n$ differing by multiples of 4. Again the same promise is held out for a simpler calculation of matrix elements.

The chains of groups described for pure configurations may be extended into mixed configurations but today I want to mention only two types of mixing, both of which are, in a sense, natural. It is quite remarable that the two simple central fields which serve as first approximations

TABLE III.

*The $J_\lambda T_\lambda$ (or $J_\mu T_\mu$) values in a factorised classification of the $j^n$ shell. (From Elliott and Evans). The entries give the values of $J_\lambda$ (or $J_\mu$).*

| $j$ \ $T_\lambda$ | 0 | $\frac{1}{2}$ | 1 | $\frac{3}{2}$ | 2 |
|---|---|---|---|---|---|
| $\frac{1}{2}$ | $\frac{1}{2}$ | 0 | | | |
| $\frac{3}{2}$ | 2 | $\frac{3}{2}$ | 0 | | |
| $\frac{5}{2}$ | $\frac{9}{2}, \frac{3}{2}$ | 4, 2 | $\frac{5}{2}$ | 0 | |
| $\frac{7}{2}$ | 2, 4, 5, 8 | $\frac{3}{2}, \frac{5}{2}, \frac{9}{2}, \frac{11}{2}, \frac{15}{2}$ | 2, 4, 6 | $\frac{7}{2}$ | 0 . |

in atoms and nuclei both have « accidental degeneracies ». I refer to the hydrogenic spectrum with degeneracies

$$1s,\ 2s2p,\ 3s3p3d,\ 4s4p4d4f, \text{ etc.},$$

and the harmonic oscillator spectrum with degeneracies

$$0s,\ 0p,\ 0d1s,\ 0f1p,\ 0g1d2s, \text{ etc.}$$

This degeneracy is due to a deeper symmetry of the two Hamiltonians which is described by the groups $R_4$ and $SU_3$ respectively. In addition to the three angular momentum operators, the generators of the group $R_4$ contain the three components of the Runge-Lenz vector

$$\boldsymbol{A} = \frac{1}{\sqrt{-8mE}} \{(\boldsymbol{p} \wedge \boldsymbol{l}) - (\boldsymbol{l} \wedge \boldsymbol{p}) - 2mZe^2\boldsymbol{r}/r\},$$

while $SU_3$ contains the five components of the second rank tensor

$$Q_q^2 = \sqrt{\frac{4\pi}{5}} \left(\frac{m\omega}{\hbar^2}\right) \left\{ r^2 Y_q^2(\theta_r \varphi_r) + \frac{\hbar^2}{m^2\omega^2} p^2 Y_q^2(\theta_p \varphi_p) \right\}.$$

In the same way that one constructs the total angular momentum $L = \sum_{i=1} l(i)$ so one may construct the other generators for the $n$-particle system and so classify the states of $n$ particles in a degenerate single particle level according to representations of the group appropriate to the single particle degeneracy.

The group $SU_3$ has been used extensively in light nuclei (see Harvey [8]). The significant feature of the representations $(\lambda\mu)$ is that the $L$-values within a given representation fall into finite rotational bands, i.e. with maximum value of $L$. Furthermore the « quadrupole force » $\sum_{i<j} (\mathfrak{Q}^{(2)}(i) \cdot \mathfrak{Q}^{(2)}(j))$, evaluated in a degenerate oscillator configuration like $(0d \text{ or } 1s)^n$, leads to a rotational spectrum with energies proportional to $L(L+1)$. In fact, many nuclei do have rotational features due to a strong « quadrupole force » in the effective nuclear interaction but there are many other components in the interaction which tend to destroy the $SU_3$ coupling. Whether the rotational bands do cut off at the maximum $L$ predicted by this model is a matter yet to be decided experimentally.

Some preliminary investigations [9] into the use of the group $R_4$ to classify states of degenerate atomic configurations, like $(2s, 2p)^n$ or $(3s, 3p, 3d)^n$ have been made, with some promising results. For example, the strong mixing of $|(2s)^2\,{}^1S>$ and $|(2p)^2\,{}^1S>$ in BeI appears to be very close to that of a pure $|(00)^1S>$ function in the $R_4$ classification.

It is perhaps important to remark that the validity of the $SU_3$ scheme in practice depends on the single particle energies and that for realistic interactions the validity is greater if the single-particle degeneracy is split. For example, one appears to be closer to $SU_3$ in the nuclear $sd$-shell, where empirically the $d$ level lies about 1 MeV above the $s$, than in the $pf$-shell where the two levels are much closer. This feature is due to the fact that the Casimir operator for $SU_3$ involves a quadrupole term $\sum_i \sum_j (\mathfrak{Q}^{(2)}(i) \cdot \mathfrak{Q}^{(2)}(j)$ which has single-particle terms in addition to the two-body quadrupole force. The same remark applies to the validity of $R_4$ in atomic structure.

A natural form of configuration mixing which is not connected with these « accidental » degeneracies may be achieved by extending the concept of seniority in a $j^n$ shell to a collection of degenerate shells $j_1, j_2, \ldots$, etc., using the group $Sp_{\sum_i (2j_1+1)}$. If the levels are non-degenerate one loses the exact group theoretic method but an approximate solution, with the same physical character of $J=0$ pairing, may be achieved [10] by using the *B.C.S.* or Bogolubov method of quasi-particles with the number of quasi-particles corresponding to the seniority.

I have restricted my discussion to compact groups, with finite dimensional irreducible representations. For one thing they are much better understood mathematically than the non-compact groups. Also within

a shell structure each configuration necessarily has a finite dimension. However, there is an infinite number of configurations and in both atoms and nuclei the mixing of configurations is large. One should clearly study the use of non-compact groups.

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M. VERDE (*)

# The Coupling Problem for Infinite-Multiplets.

Atomic as well as nuclear and elementary particles spectroscopy, according to the generous amount of experimental information that we possess today, show some similarities disclosing perhaps a common origin. Let us, for instance, remember the important phenomenon of degeneracy in the ordering of quantum states i.e. the so called multiplets. These are sets of states belonging exactly or almost exactly to the same value of an observable like energy, mass, or angular momentum.

The simplest situation occurs when the number of components of a multiplet is finite, but multiplets with an infinite number of components, e.g. those forming a band spectrum, are also quite common.

A multiplet structure, as it is well known, reveals the presence of a certain symmetry or of some invariance property of a given observable with respect to transformations of the dynamical variables that serve to define it. When these transformations simultaneously involve coordinates and momenta, they sustain the ambitious hopes of those who try to offer a geometrical description of a dynamical problem.

In this connection the multiplet structure present in the spectrum of hydrogen atoms offers the first intriguing example. The occurrence of the Lenz-Pauli integral of motion besides the angular momentum integral common to all other central symmetric problems, explains the $n^2$ components of the multiplet belonging to a level $E_n$, i.e. the $n$ states with an angular momentum from zero to $n - 1$. The product of two commuting three-dimensional rotations yields the structure of a rotation in a four-dimensional space.

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In his celebrated paper of 1935, V. Fock [1] showed not only that o(4) was the maximal group of degeneracy of the hydrogen atom but also that the continuum states could be associated with irreducible unitary representations of the Lie-algebra o(2,1) which is composed of all linear and real three-dimensional pseudo-rotations that leave invariant the quadratic form: $x^2 + y^2 - t^2$, i.e. a three-dimensional Lorentz-group.

This is a non-compact group whose unitary respresentations have matrix elements with a discrete infinite number of rows and columns if a subgroup o(2) is chosen diagonal. Each row or column forms an infinite multiplet.

The evaluation of the electromagnetic transition probabilities in the hydrogen atom requires a large use of the non-compact algebra associated with the direct product of two commuting o(2,1). This means that we have to solve the coupling problem of two or more infinite multiplets. First of all it becomes necessary to compute explicitly all possible matrix elements formed by the product of three multiplets of o(2,1).

For o(3) this corresponds to the evaluation of the well known Clebsch-Gordan coefficients or Wigner 3-$j$ coefficients.

The groups o(4) and o(2,1) are subgroups of the larger de-Sitter group which arises when one combines the orthogonal transformations in a four-dimensional space with translations, scale transformations and inversions [2].

More recently [3] it has been realized that the still larger group o(4,2) of conformal relativity, the largest invariance group of the Maxwell equations, can be assumed to form the dynamical group of the hydrogen atom in interaction with an external electromagnetic field.

I wish to add that o(2,1) allows the classification of the collective vibrational states of a collection of particles moving in a one-dimensional harmonic oscillator well [4]. The different components of an infinite multiplet of o(2,1) correspond to different values of a vibrational degree of freedom. Each multiplet forms a vibrational band characterized by the same value of the Casimir invariant of o(2,1).

More generally as emphasized especially by H. J. Lipkin, the Lie-algebra of N boson-states formed by all possible bilinear products of creation and destruction operators is isomorphic to a unimodular $N$ dimensional group for the set of operators which leave the total number of particles unchanged and to a $2N$ dimensional symplectic group for those combinations which create or eliminate pairs of particles. The classification of states according to the unitary group leads to the collective rotational states familiar from the nuclear shell model of Elliott [5], whereas

the other group of transformations i.e. the symplectic one, which is a particular contact-transformation, gives rise to a combination of vibrational-rotational collective states. These considerations are relevant for the role that infinite-multiplets may have in nuclear spectroscopy. Moreover a similar situation appears in the ordering of the many hadronic excited states in elementary particles spectroscopy after the suggestion of M. Gell-Mann, Y. Neeman and others [5].

Finally o(2,1) is the little or stability group of the Poincaré group referring to space-like momenta and therefore is also relevant in those scattering problems where the squared momentum transfer is negative.

The ultimate goal of our research is an attempt to extend all of the Racah-Wigner calculus, the powerful mathematical tool which has allowed the beautiful unraveling of the most complex atomic spectra and provides the means for calculating probability amplitudes when the three-dimensional rotational symmetry is working, to the non compact Lie-algebras especially those associated with pseudorotations.

This is still an ambitious program full of difficulties essentially stemming from the fact that the Casimir operators of non-compact groups are not positive definite. The irreducible unitary representations of the group generators are a partly continuous set of matrices of infinite dimensions [6].

The foundation of the Racah-Wigner calculus is twofold. The Wigner coupling coefficients which allow us to build irreducible tensors from the product of two of them, and the Racah recoupling coefficients which serve for the labelling of all the irreducible components in the product space of several irreducible representations. Yet, the definition and the effective calculation of the Wigner coupling coefficients, their symmetry properties, represent the central issue of the entire question.

I wish to report on some results recently obtained in the explicit evaluation of the matrix elements of the product of three infinite multiplets of o(2,1) together with a treatment of all their symmetry properties.

I am glad to affirm that in our modest piece of work, the general aim of this meeting celebrating the Mendeleevian discovery, is respected in a certain sense, since the notions of periodicity and symmetry play an important role in it. Periodicity is indeed so intimately connected with almost all quantum numbers and symmetry has so large a part in that well known mathematical device, called analytic continuation, that enters in a basic manner in our attempt to extend the illuminating results of the compact Lie-algebras to the algebra of infinite multiplets.

## 1. The product of three multiplets of $SU(1.1)$.

Let us begin by cosidering the Bargmann [6] function

$$(\mathrm{1})\quad d^j_{\nu,\mu}(A) = N^j_{\nu,\mu} \frac{\alpha^{-(\nu+\mu)}\gamma^{(\nu-\mu)}}{\Gamma(1+\nu-\mu)} {}_2F_1\left(\frac{1}{2}+j-\mu, \frac{1}{2}-j-\mu;\ 1+\nu-\mu;\ -\beta\gamma\right)$$

$$N^j_{\nu,\mu} = \sqrt{\frac{\Gamma(1+2\nu)}{\Gamma(1+2\mu)} \frac{B\left(\frac{1}{2}+j+\nu, \frac{1}{2}-j+\nu\right)}{B\left(\frac{1}{2}+j+\mu, \frac{1}{2}-j+\mu\right)}}$$

$$B(r, s) = \frac{\Gamma(r)\Gamma(s)}{\Gamma(r+s)}\,.$$

The four parameters $\alpha$, $\beta$, $\gamma$, $\delta$ are the elements of a two-dimensional unimodular matrix

$$(2)\qquad A = \begin{pmatrix}\alpha & \beta\\ \gamma & \delta\end{pmatrix} \qquad \alpha\beta - \gamma\delta = 1\,.$$

After their definition the functions $d^j$ can be written in integral form as follows:

$$(3)\qquad d^j_{\nu,\mu} = \frac{N^j_{\nu,\mu}\alpha^{-(\nu+\mu)}\gamma^{(\nu-\mu)}}{\Gamma\left(\frac{1}{2}+j-\mu\right)\Gamma\left(\frac{1}{2}-j+\nu\right)}\,\cdot$$

$$\cdot\int_0^1 s^{-\frac{1}{2}+j-\mu}(1-s)^{-\frac{1}{2}-j+\nu}(1+\beta\gamma s)^{-\frac{1}{2}+j+\mu} ds\,.$$

In order to consider arbitrary values of the quantum numbers $j$, $\nu$, $\mu$ it is also convenient to follow the suggestion by B. Riemann and L. Pochhammer consisting of the shift of the integration's path to a closed contour that avoids the singularities of the integrand. One has simply to put

$$\int_{s_1}^{s_2} (s-s_1)^{\lambda_1}(s-s_2)^{\lambda_2} f(s)ds = \frac{\oint_{\Gamma_d}(s-s_1)^{\lambda_1}(s-s_2)^{\lambda_2}ds}{(1-e^{2i\pi\lambda_1})(1-e^{2i\pi\lambda_2})}$$

where $\Gamma_d$ is a double loop as it is indicated in the fig. 1. As it is well known the integral representations of the functions $d^j_{\nu,\mu}$ offers also the most convenient way for evaluating their asymptotic behaviour for large $|j|$. We are interested in considering integer values for the difference $\nu-\mu$

of the magnetic quantum numbers. Since the integrand in eq. (3) resumes then its initial value after the integration's variable has described a single loop, we get the simpler integral

$$d^j_{\nu,\mu}(A) = \overline{N}^j_{\nu,\mu} \frac{1}{2i\pi} \oint_{\Gamma_s} t^{-\frac{1}{2}-j+\nu} (\alpha t + \gamma)^{-\frac{1}{2}+j-\mu} (\beta t + \delta)^{-\frac{1}{2}+j+\mu} dt$$

$$\overline{N}^j_{\nu,\mu} = \sqrt{\frac{\cos \pi(j-\mu)}{\cos \pi(j-\nu)} \frac{B\left(\frac{1}{2}+j+\nu, \frac{1}{2}+j-\nu\right)}{B\left(\frac{1}{2}+j+\mu, \frac{1}{2}+j-\mu\right)}}$$

where $\Gamma_s$ is the path of fig. 2.

For $\gamma = -\overline{\beta}$, $A$ of eq. (2) becomes a matrix of $SU(2)$, whereas for $\gamma = \overline{\beta}$, $A$ is istead a matrix of $SU(1,1)$. It is now sufficient to restrict

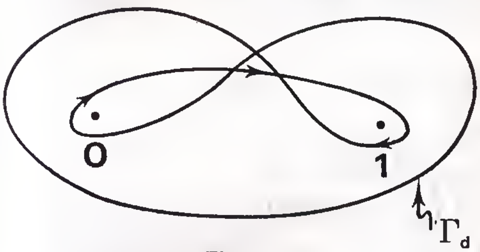


Fig. 1.

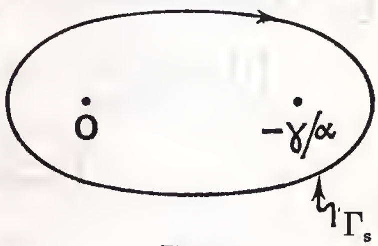


Fig. 2.

the values of the quantum numbers $j$, $\nu$, $\mu$ to those belonging to the spectrum of $SU(2)$ respectively $SU(1,1)$ for obtaining each time a unitary representation of the corresponding group. We stress the importance of the common origin of both representations in order to carry out our program of complexification of the $3-j$ coupling coefficients from the compact group $SU(2)$ to the non-compact $SU(1,1)$. Our task consists of the evaluation of the invariant integral

$$\int_\Omega d^{j_1}_{\nu_1\mu_1}(A) d^{j_2}_{\nu_2\mu_2}(A) d^{j_3}_{\nu_3\mu_3}(A) dA$$

over the group manifold $\Omega$ of $SU(1,1)$. The corresponding case of $SU(2)$ is well established.

With the parametrization

$$\alpha = Ch \frac{\sigma}{2} e^{i\frac{\varphi+\psi}{2}} \qquad \beta = Sh \frac{\sigma}{2} e^{i\frac{\varphi-\psi}{2}} \qquad 0 \leq \sigma \leq \infty$$

the integration over the Euler's angles $\varphi$, $\psi$ is trivial, so that we may restrict our attention to the following integral:

$$I = \int_1^{\infty} dz \left( \prod_1^3 {}_k \, d^{j_k}_{\nu_k, \mu_k}(z) \right) \tag{4}$$

$j_k$, $\nu_k$, $\mu_k$ being on the spectrum of $SU(1,1)$ and $\nu_1 + \nu_2 + \nu_3 = \mu_1 + \mu_2 + \mu_3 = 0$, $z = Ch\sigma$.

The most interesting situation arises when both $j_1^2$ amd $j_2^2$ are negative i.e. when both of them belong to the continuous spectrum of $SU(1,1)$. In this case the value of I eq. (4) can be espressed as follows [7]:

$$I = \begin{bmatrix} j \\ \nu \end{bmatrix} \cdot \begin{bmatrix} j \\ \mu \end{bmatrix} + \begin{bmatrix} -j \\ \nu \end{bmatrix} \cdot \begin{bmatrix} -j \\ -\mu \end{bmatrix} \tag{5}$$

$\begin{bmatrix} j \\ \nu \end{bmatrix}$ is a short notation for a $3-j$ symbol defined by

$$\begin{bmatrix} j \\ \nu \end{bmatrix} = \begin{bmatrix} j_1 \, j_2 \, j_3 \\ \nu_1 \, \nu_2 \, \nu_3 \end{bmatrix} = \alpha(j_1, \nu_1)\alpha(j_2, \nu_2)\alpha(-j_3, -\nu_3)\omega(j_1, j_2, j_3) \cdot$$

$$\cdot \sqrt{\frac{\pi}{sin 2\pi j_2}} \cdot \frac{F p_\nu(0)}{\Gamma\left(\frac{1}{2} - j_2 + \nu_2\right)}$$

where

$$\alpha(j, \nu) = \sqrt{\frac{\Gamma\left(\frac{1}{2} - j + \nu\right)}{\Gamma\left(\frac{1}{2} - j - \nu\right)}}$$

$$\omega(j_1, j_2, j_3) =$$

$$= \sqrt{\Gamma\left(\frac{1}{2} + j_1 + j_2 + j_3\right) \Gamma\left(\frac{1}{2} - j_1 + j_2 + j_3\right) \Gamma\left(\frac{1}{2} + j_1 + j_2 - j_3\right) \Gamma\left(\frac{1}{2} - j_1 + j_2 - j_3\right)}$$

and $F p_\nu(0)$ is the hypergeometric function with unit argument [8]

$$F p_\nu(0) = \frac{1}{\Gamma\left(\frac{1}{2} + j_1 + j_2 + j_3\right) \Gamma(1 + j_2 - j_1 + \mu_3) \Gamma(1 + j_2 - j_3 - \mu_1)} \cdot$$

$$\cdot \, {}_3F_2 \begin{bmatrix} \frac{1}{2} - j_1 - \nu_1 & \frac{1}{2} - j_3 + \nu_3 & \frac{1}{2} - j_1 + j_2 - j_3 \\ & 1 + j_2 - j_1 + \mu_3 \quad 1 + j_2 - j_3 - \mu_1 & \end{bmatrix}.$$

$Fp_\nu^j$ and $Fp_\nu^{-j}$ have a common domain of holomorphy defined by

$$-\frac{1}{2}-Re(j_1+j_2)\leq Rej_3\leq\frac{1}{2}-Re(j_1+j_2)\,.$$

They can be continued analytically outside this strip which is also independent of the value of $\nu$.

The derivation of eq. (5) rests on some essential points on which I wish now to comment briefly.

As in the similar but simpler situation in the theory of Fourier integrals, the functions $d^j_{\nu,\mu}$ can be expressed as a difference of two functions each of them being holomorphic in a half-plane. For the half-plane $Rej>0$ this function can be chosen to be

$$e^j_{\nu,\mu}=a^j_{\nu,\mu}\left(\frac{1}{z-1}\right)^{\lambda+\frac{1}{2}}\left(\frac{z+1}{z-1}\right)^{-\frac{\nu+\mu}{2}}F\left(\frac{1}{2}+j-\nu,\frac{1}{2}+j-\mu,1+2j;\frac{2}{1-z}\right)$$

where

$$a^j_{\nu,\mu}=\frac{2^{j+\frac{1}{2}}}{\Gamma(1+2j)}\cdot$$

$$\cdot\sqrt{\frac{\cos\pi(j+\mu)}{\cos\pi(j+\nu)}\Gamma\left(\frac{1}{2}+j+\mu\right)\Gamma\left(\frac{1}{2}+j-\mu\right)\Gamma\left(\frac{1}{2}+j+\nu\right)\Gamma\left(\frac{1}{2}+j-\nu\right)}\,.$$

For large $|j|$ $Rej>0$ it is [9]

$$e^j_{\nu,\mu}\simeq e^{\pm i\frac{\pi}{2}(\nu-\mu)}\sqrt{\frac{2\pi}{jSh\sigma}}\,e^{-\sigma i}\qquad Imj\gtrless 0,\ z=Ch\sigma$$

and

$$d^j_{\nu,\mu}(z)=-\frac{1}{j}\,\frac{e^j_{\nu,\mu}(z)-e^{-j}_{\nu,\mu}(z)}{a^j_{\nu,\mu}a^{-j}_{\nu,\mu}}=-\frac{1}{j}\,\frac{e^j_{\nu,\mu}(z)-e^{-j}_{\nu,\mu}(z)}{\frac{1}{2i\pi}\oint_C e^j_{\nu,\mu}(z)e^{-j}_{\nu,\mu}(z)dz}\,.$$

The integration's path $C$ is a closed contour in the complex $z$ plane which encircles the two singular points $z=\pm 1$ and it is described counterclockwise.

There is now an important property satisfied by the set of functions $e^{j+n}_{\nu,\mu}(z)$ with $n$ an arbirary negative or positive integer, and the corresponding dual set $e^{-j-n}_{\nu,\mu}(z)$. Namely they form a complete biorthogonal basis in their common domain of holomorphy. Every analytic function $f(z)$ in

that domain, having the same branching around $C$ as $e^j_{\nu,\mu}$, can be expanded uniformly in every compact subdomain by the series:

$$(6) \qquad f(z) = \sum_{-\infty}^{+\infty}{}_n C_n e^{j+n}_{\nu,\mu}(z) \bigg/ \frac{1}{2i\pi} \oint e^{j+n}_{\nu,\mu}(t) e^{-j-n}_{\nu,\mu}(t) dt \,.$$

Due to the previously mentioned orthogonalization of the $e^j_{\nu,\mu}$ 's, the coefficients $C_n$ are given by

$$C_n = \frac{1}{2i\pi} \oint_C f(z) e^{-j-n}_{\nu,\mu}(z) \,.$$

If we apply this expansion property to the product $e^{j_1}_{\nu_1,\mu_1} \cdot e^{j_2}_{\nu_2,\mu_2}$ we perform a reduction of the direct product of two irreducible representations of $SU(1,1)$ to a simple sum of irreducible representations. Yet, this reduction is still not of the type necessary to define a complete set of Wigner's coupling coefficients, since the $e^j_{\nu,\mu}$ 's do not form a unitary representation. The spectrum of $SU((1,1)$ is partly continuous and partly discrete whereas the sum in eq. (6) is discrete. It remains to transform the series into a Stieltjes integral over the spectrum of $SU(1,1)$. This is indeed possible by means of a Sommerfeld-Watson transform [7]. It is in this way that we deduce the result anticipated in eq. (5).

The negative axis of $j_2^2$ is a branching line for $\begin{bmatrix} j \\ \nu \end{bmatrix}$ and if we consider the two values of this symbol on the upper and lower border of the branching line they form a basis for a monodromy group which serve to define them.

## 2. The Symmetry properties of the $\begin{bmatrix} j \\ \nu \end{bmatrix}$ symbols.

The fact that we have to consider both of these values in the reduction of two infinite multiplets brings a new feature which is not common to the $SU(2)$ case. Since we have to accept the new coupling coefficients as an analytic continuation from $SU(2)$ which is a multiplicity free case, it becomes interesting to investigate how our symbols $\left(\begin{bmatrix} j \\ \nu \end{bmatrix}, \begin{bmatrix} -j \\ \nu \end{bmatrix}\right)$ behave under permutations of any pair of quantum numbers $(j_k, \nu_k)$. Let us i.e. shortly indicate a permutation of 1 and 2 by $P_{12}$

$$\begin{bmatrix} j_2 \, j_1 \, j_3 \\ \nu_2 \, \nu_1 \, \nu_3 \end{bmatrix} = P_{12} \begin{bmatrix} j_1 \, j_2 \, j_3 \\ \nu_1 \, \nu_2 \, \nu_3 \end{bmatrix} .$$

Putting

$$S = \begin{bmatrix} j \\ \nu \end{bmatrix} \begin{bmatrix} j \\ -\mu \end{bmatrix} + \begin{bmatrix} -j \\ \nu \end{bmatrix} \begin{bmatrix} -j \\ -\mu \end{bmatrix} \tag{7}$$

it must be verified that

$$P_{h,k} S = S \qquad (h, k = 1, 2, 3).$$

Yet, this does not necessarily imply that each symbol $\begin{bmatrix} j \\ \nu \end{bmatrix}$ is also separately invariant. It is indeed possible to deduce that

$$P_{h,k} = \begin{pmatrix} \begin{bmatrix} j \\ \nu \end{bmatrix} \\ \begin{bmatrix} -j \\ \nu \end{bmatrix} \end{pmatrix} = \Omega^j_{h,k} \begin{pmatrix} \begin{bmatrix} j \\ \nu \end{bmatrix} \\ \begin{bmatrix} -j \\ \nu \end{bmatrix} \end{pmatrix}$$

where $\Omega_{h,k}$ are two-dimensional matrices, that for $\nu - \mu$ integer happen to be independent from the values of $\nu$. These matrices are also symmetric under the exchange of rows with columns and satisfy the conditions:

$$\text{Trace } \Omega^j_{h,k} = 0 \qquad \text{Det. } \Omega^j_{h,k} = -1\,. \tag{8}$$

The matrices $\Omega$ are however not diagonal. This is also the case under an operation $I$ of inversion of all three signs of the $\nu$ 's.

Under this operation

$$\begin{pmatrix} \begin{bmatrix} j \\ -\nu \end{bmatrix} \\ \begin{bmatrix} -j \\ -\nu \end{bmatrix} \end{pmatrix} = I \begin{pmatrix} \begin{bmatrix} j \\ \nu \end{bmatrix} \\ \begin{bmatrix} -j \\ \nu \end{bmatrix} \end{pmatrix} = O^j \begin{pmatrix} \begin{bmatrix} j \\ \nu \end{bmatrix} \\ \begin{bmatrix} -j \\ \nu \end{bmatrix} \end{pmatrix}$$

the matrix $O^j$ is symmetric and shares with the $\Omega^j_{h,k}$ 's the same properties expressed by eq. (8). This ensures the validity of $IS = S$, as it must clearly be.

The product of any permutation $P_{h,k}$ with the inversion $I$ leaves invariant the $3 - j$ coefficients of $SU(2)$. In the complexification of our coupling coefficients this is a property that can be asked to be mantained at least for some permutations. It is easy to verify, with the same kind of considerations already presented elsewhere [7], that our symbols $\begin{bmatrix} j \\ \nu \end{bmatrix}$, $\begin{bmatrix} -j \\ \nu \end{bmatrix}$ satisfy the condition

$$P_{13} \cdot I = (-)^{\nu_2}\,. \tag{9}$$

This inconvenience can be easily be amended by modifying our symbols with an appropriate phase factor. Since the product in eq. (7) is invariant under suitable orthogonal transformations in the two dimensional space of the two coefficients $\left(\begin{bmatrix} j \\ \nu \end{bmatrix}, \begin{bmatrix} -j \\ \nu \end{bmatrix}\right)$ the definition of the new $3-j$ symbols is open to different choices. One way to fix them is the requirement that if the two initial multiplets are eigenstates of a certain operator $\Omega$ ($\Omega^2 = 1$) the direct product of them continues to be so. The operator $\Omega$ should correspond to a kind of charge conjugation.

According to the conditions expressed by eqs. (8) and (9) the complete determination of the matrices

$$\Omega_{h,k} = \begin{pmatrix} a_{hk} & b_{hk} \\ c_{hk} & d_{hk} \end{pmatrix} \qquad \text{and} \qquad O = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

is reached with the values:

$$\begin{cases} a_{12} = -\left[\cos \pi(-j_1 + j_2 + j_3) \cos \pi(j_1 - j_2 + j_3)/\sin 2\pi j_1 \sin 2\pi j_2\right]^{\frac{1}{2}} \\ b_{12} = \quad \left[-\cos \pi(j_1 + j_2 + j_3) \cos \pi(j_1 + j_2 - j_3)/\sin 2\pi j_1 \sin 2\pi j_2\right]^{\frac{1}{2}} \end{cases}$$

$$\begin{cases} a_{23} = -\left[\cos \pi(j_1 - j_2 + j_3) \cos \pi(j_1 + j_2 - j_3)/\sin 2\pi j_2 \sin 2\pi j_3\right]^{\frac{1}{2}} \\ b_{23} = \quad \left[-\cos \pi(j_1 + j_2 + j_3) \cos \pi(-j_1 + j_2 + j_3)/\sin 2\pi j_2 \sin 2\pi j_3\right]^{\frac{1}{2}} \end{cases}$$

$$a = \frac{A(j,\nu)}{A(j,-\nu)} \frac{K(j,\nu)}{C(j,\nu)} \qquad b = -\frac{A(j,\nu)}{A(-j,-\nu)} \frac{B(j,\nu)}{C(j,\nu)}$$

$$A(j,\nu) = \begin{bmatrix} j \\ \nu \end{bmatrix} \Big/ F p_\nu(0)$$

$$B(j,\nu) = 1/\Gamma\left(\frac{1}{2} + j_2 - \nu_2\right) \Gamma\left(\frac{1}{2} + j_2 + \nu_2\right) \Gamma\left(\frac{1}{2} + j_1 + j_2 + j_3\right) \cdot$$
$$\cdot \Gamma\left(\frac{1}{2} + j_1 + j_2 - j_3\right) \Gamma\left(\frac{1}{2} - j_1 + j_2 + j_3\right) \Gamma\left(\frac{1}{2} - j_1 + j_2 - j_3\right)$$

$$C(j,\nu) = \frac{\sin 2\pi j_2}{\pi} \Big/ \Gamma\left(\frac{1}{2} - j_3 - \nu_3\right) \Gamma\left(\frac{1}{2} + j_3 - \nu_3\right) \Gamma\left(\frac{1}{2} + j_1 + \nu_1\right) \Gamma\left(\frac{1}{2} - j_1 + \nu_1\right)$$

$$\pi^3 K(j,\nu) = \cos \pi(j_2 + \nu_2) \cdot \cos \pi(j_1 - j_2 + j_3) \cdot \cos \pi(j_1 + j_2 - j_3) +$$
$$+ \sin 2\pi j_2 \cdot \sin \pi(j_2 - j_3 - \nu_1) \cdot \cos \pi(j_3 + \nu_3) .$$

The coupling problem of $SU(1,1)$ can therefore be said to have been solved apart from a further orthogonal transformation which is the object of a further investigation.

Looking back to our procedure we may conclude that there is a way for reaching a unified treatment of the two groups $SU(2)$ and $SU(1,1)$ not only for the matrix elements of the unitary irreducible representations but also for the coupling coefficients. This has been achieved by means of a suitable chain of irreducible non unitary representations which form a complete set of biorthogonal functions, which we have called $e^{j+n}_{\nu,\mu}$.

Finally I wish to mention that L. Pukanszky [12], M. Andrews and J. Gunson [11] and more recently also W. J. Holman and L. C. Biedenharn [13] have worked in the same field with results that only in part overlap with ours.

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MURRAY GELL-MANN (*)

# The Value of Schemes in Scientific Theory.

I would like to begin by congratulating the organizers of this conference on selecting its topic in such an ingenious manner. It would have been easy to celebrate this centenary of the Mendeleev chart with a conference narrowly devoted to the same subject. But how refreshing to have realized that one can better appreciate the work of Mendeleev by looking at it in a larger context — by taking as the subject viewpoints that have emerged in the last century in the search for a basic understanding of the microscopic laws of physical science. This search has carried us to successively smaller and smaller distances, revealing whole areas of science on our way. Thus we have passed from chemistry to atomic physics, to nuclear physics, and finally to particle physics, which, for the moment, is the end of the series.

I was originally asked to summarize the century's work in these fields but I feel that that would be inappropriate for me because my background in the history of science is very weak and I would inevitably say many foolish things. I have decided instead to do something which is even worse, to try to place the subject matter of this conference in an even wider context by generalizing still further the notions of periodicity and symmetry that inspired the outline of the meeting. I would like to discuss the general subject of all preliminary phenomenological schemes for the arrangements of facts in science. The topics of periodicity and symmetry become then only special cases of this more general one.

By such preliminary schemes, I mean to include the perception of apparent patterns in the data, the arrangement of facts into provisional structures, and the construction of phenomenological theories or rules. At the time of constructing such a scheme, one is guided mainly by the data, and not by deep reasoning from theoretical principles or from underlying dynamical arguments. One hopes that in the future the deficiencies in understanding will be remedied, that one will eventually find the theoreti-

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cal insights and dynamical arguments. In the meantime, one settles for a scheme which is less fundamental but which may nevertheless be effective for a long time.

We can see the operation of that method of procedure in the topics discussed during both halves of this meeting. The work of Mendeleev himself is an obvious example, but so also are the many kinds of schemes with which people have been concerned in nuclear physics, such as the single particle model with j-j coupling. There are a number of examples in particle physics, in formulating some of which I have participated, such as the work on strangeness or the eightfold way. It is very tempting to arrange the known facts — sometimes even discarding a few as possibly being experimental errors — in a pattern to see whether one can not extract from the pattern a set of verifiable predictions. This last idea is, of course, the important one; it is essential to construct a scheme that has genuine predictive power.

The schemes alluded to above and others to which we will return later are slightly mathematical in nature because they are concerned with physics and chemistry. It is possible to find examples of phenomenologial schemes in quite different fields. I would like to draw parallels between what Mendeleev did in a very quantitative science and the work of Charles Darwin in a science that at the time was mainly qualitative.

Darwin constructed his scheme of evolution without any accurate notion of the mechanism underlying it. In fact, it took decades before two of the primary mechanisms were elucidated. Darwin knew nothing either of genetics or of the dynamics of mutations, and yet arrived at an essentially correct picture of evolution. In the same way, the time lag for Mendeleev's field was very great since the dynamical explanation underlying the periodic chart did not come untile the invention of quantum mechanics and its subsequent application to the study of atomic systems with electrical forces. Thus a considerable gain in time was made by advancing the chart without waiting sixty years for its dynamical explanation.

The reason that I take the trouble to mention these obvious parallels is that I would like to spread propaganda against some trends that have been apparent in many branches of science during this generation. These trends are inspired, I think, by something very noble — a desire to achieve something more worthwhile than the schemes we have been discussing, and in particular, to emulate the achievement of Newton in crowning the work of Galileo and Kepler.

Newton constructed a theory tha texplained a great many observations but was basic and dynamical and thus completely satisfying. The universal law of gravitation coupled with the laws of motion made up an almost complete description of gravitational systems, which was to be modified

only by Einstein's subsequent introduction of special and general relativity. For hundreds of years after Newton, all work in the subject was deductive, and every worker had to pay tribute to Newton's basic theory. In a sense it is certainly true that this kind of accomplishment deserves more credit than, say, the work of Darwin, which while very great did not represent a complete dynamical description of the system under consideration.

Is that any reason for our generation to put so much faith in the attempt to emulate Newton? Enormous prestige attaches today to such sophisticated constructs as dynamical models, or computer models in the case of complicated systems, or theories employing fancy mathematics (often much fancier than the facts or the insights in the particular field would support). Much less prestige adheres to the modest phenomenological approach even when it shows promise of making considerable provisional advances. This, I think, is a mistake.

After all, not all of us have the opportunity in our respective scientific endeavors to construct at every moment something on the Newtonian scale. The opportunity to make modest contributions in a phenomenological way comes more often. It may be that we should encourage ourselves, our friends, and our younger colleagues to think in terms of seizing this kind of opportunity at times when the general dynamical synthesis in the Newtonian manner is not so easy to accomplish.

I would like now to move from the historical figures of Mendeleev and Darwin to two contemporary cases in physical science, one from geophysics and the other from astrophysics, which illustrate some of the points I have been making. Since this talk is essentially a sermon, I shall present these cases in the traditional highly distorted way to serve as examples for the sermon, while adding those additional distortions that come from my ignorance of both fields.

The first example is concerned with the current revolution in geophysics. A couple of generations ago, Wegener proposed an ingenious scheme which referred to continental drift. What he did among other things was simply to match the shape of the continental shelves and to notice that there was a possibility that hundreds of millions of years in the past certain continents (and perhaps all the continents) may have been joined together, and may have split apart in the interval. Continents would then have to be regarded as being superimposed on the earth's mantle. This was, then, a scheme of the same sort that we have discussed before. However, it was one with little immediate predictive power; the numerous predictions were all very difficult to verify.

More recently this idea, which many respectable geologists had regarded for a long time as a crank idea, was revived in connection with entirely new data stemming from studies of old magnetism. These studies revealed

first of all that the earth's magnetism over the course of time undergoes a gradual migration of the magnetic North Pole in addition to repeated reversals of polarity. Then the studies revealed that the magnetism in each continent had changed with respect to the others in following these migrations of the earth's magnetic pole. This indicated some form of continental drift, which turned out to be consistent with the old scheme of Wegener. Research and interpretation of this kind continued through the efforts of such men as Bullard and Blackett.

But these researches and interpretations were not generally accepted by geophysicists. I have been led to believe that geophysicists have debates about these issues, followed by audience voting to determine which side is correct. So we may imagine an annual series of geophysical meetings in the recent past in which Bullard in favor of the idea of continental drift debated with a hypothetical theoretical opponent who argued against it. Each year, as Bullard appeared with more and more extensive observations, and proposed interpretations which had wider and wider implications for the specialized fields of the audience, the hypothetical opponent pointed out that each successive feature of the scheme lacked a dynamical mechanism, and that there was no physical basis for the production of the drift. Thus, as the evidence mounted, year by year, in favor of some form of drift, it seemed more and more implausible; the vote of the audience more and more strongly opposed it. Finally, in the year when the evidence in favor of continental drift became overwhelming, the theory was overwhelmingly defeated.

Nevertheless, the evidence for something of the kind has in fact become decisive, particularly with the discovery of the phenomenon of sea-floor spreading. This is the phenomenon in which rock emerges upward from a rift in the ocean floor and spreads out both ways from the rift, as, for example, on the floor of the mid-Atlantic. The actual observations pointing to this phenomenon are that the ocean floor rock on both sides of the rift is divided into bands of magnetism of alternating polarity. The history of the changing magnetism, read outwards in both directions from the rift, corresponds to the history of these magnetic changes available in vertical sedimentary layers elsewhere on the earth. The rate of spreading, moreover, seems to have been roughly constant for many tens of millions of years.

The original continental drift idea of Wegener has thus evolved into the rather sophisticated scheme called plate tectonics, and, bit by bit, even dynamical features of it are being uncovered. All of the following is extremely speculative but the general idea of the scheme is that a continent is part of a plate on the crust of the earth. Two of these plates are fed simultaneously, upwelling from a rift and spreading in opposite direc-

tions. What happens when two such plates meet on the other side of the earth? The notion that is being played with is that two possible things may happen depending on the relative approach velocity of the two plates. If they are approaching each other slowly, it may happen that the land buckles and gives rise to the building of gigantic mountain chains. If they are approaching each other more rapidly, it may be that one of the plates digs under the other and gives rise to a huge, deep trench with associated arcs of islands and volcanoes. Thus, implications for some of the more outstanding questions in geology arise from this scheme even if some of the details above turn out to be incorrect.

Since this is not my field, I cannot properly comment on the validity of plate tectonics; the indications seem to an outsider to be very good that these ideas are on the right track.

The hypothetical debating opponent of Bullard was making all his arguments on detailed dynamical grounds. This was a doubtful procedure, because at an early stage in a science it is premature to rely on exact dynamical calculations; the subject is, as yet, too complicated to be completely analyzed. Meanwhile, the advocates of continental drift, paying close attention to the facts and trying to arrange them in a pattern, were actually getting much closer to the provisional truth.

Let us now consider another example: the study of exotic astronomical objects. A number of mysterious, very small, very bright sources or energy have been noticed in the last few years by astronomers. They are at the extreme upper end of the observed range of luminosities, extending as high as $10^{47}$ ergs per second. At first, some of them were called « quasi-stellar radio sources » but now, with the appearance of more objects of this kind which differ among themselves, some having detectable radio signals and other not, they are all lumped together under the name « quasi-stellar objects » or « quasars ».

Lower than the quasi-stellar objects in luminosity are the curious systems referred to as radio galaxies — bright elliptical galaxies on both sides of which appear patches of radio emission. These patches range from those which are fairly close and small to those which are enormous and extend far away from the galaxy. Another set of objects consists of the strange galaxies called « Seyfert galaxies » or « N-type galaxies », which contain within them very bright sources of light and radio emission which may be very small. Our own galaxy is generally thought to possess a nucleus like others of its type. The nucleus so far is accessible to good observation only in the infrared and radio regions of the electromagnetic spectrum. It may be that inside this nucleus there is a bright point, which one might call a « nucleolus », that is emitting a continuous spectrum with an intensity of the order of $10^{38}$ ergs per second. This would make

our own galaxy similar to a «Seyfert galaxy» but on a much smaller scale.

These objects all emit continuous radiation, which is what I would like to discuss. These sources of continuous radiation are frequently surrounded by an envelope of some kind which gives rise to disCerte absorption lines. Astrophysicists have done much work on these spectral lines because they present such readily available evidence, but I do not want to concern myself with the envelopes. Let me focus on the tiny, bright, continuous spectrum sources inside these astronomical objects, many of which are very large. In particular, I am interested in the existence of possible relationships among the sources.

The question is, are the phenomenological methods of pattern-seeking useful for this problem? This is not merely a rhetorical question, for unlike the examples I have presented earlier, there is as yet no known answer for this one. No detailed scheme has yet emerged. One way to start looking for patterns among the sources is to see whether we can arrange some or all of them in a sequence according to certain parameters.

Speaking of objects within the class of the radio galaxies alone, people have suggested that they may be arranged in an evolutionary sequence, that is according to the parameter, of the age of the radio galaxy. Perhaps the galaxies in which the two patches of noise are close together and small are young, and those in which they are far apart and diffuse are older. Of course there may be other parameters in addition to the age which affect the characteristics of the system, and these would also have to be plotted, but this glimmering of a phenomenological scheme for a narrow class of objects may give us encouragement.

Let us explore the question a bit further. Can the quasi-stellar objects be put into this same sequence? Do they have any connection with something inside the radio galaxies? Some people have suggested that inside the bright elliptical galaxy which forms the center of the radio galaxy system there was a very intense source which flared up at one time and gave rise to the patches of radio noise which have since drifted apart. Could that initial flaring source have been a tiny one such as a quasi-stellar object? This is not yet known, but in order for it to be true we must establish some positional connection between quasi-stellar objects and galaxies.

The question is made more difficult by the observation that for one or two nearby quasi-stellar objects there is no bright surrounding galaxy. However, most of the quasi-stellar objects are so far away that even a bright surrounding galaxy, if present, could not be seen, so that we would have no way of knowing directly whether these objects are inside galaxies. The next step is to ask whether they occur, like galaxies, in clusters of

galaxies. This question has been discussed for a number of years at Caltech. Maarten Schmidt, who played a leading role in the discovery of quasars, has attempted to see whether there is a correlation in the apparent space directions of the quasi-stellar objects and those of clusters of galaxies. A recent paper by John Bahcall, Maarten Schmidt, and James Gunn gives preliminary evidence that some entities previously classified as quasi-stellar objects are associated directionally with clusters of galaxies.

If it turns out to be true that quasars generally exist in clusters of galaxies, there would be two important consequences. First of all, their presence in clusters of galaxies would confirm the other evidence that these quasi-stellar objects are very far away. (Without such confirmation, some astrophysicists have kept harping on the possibility that quasars might be, so to speak, only a block away). Secondly, their presence in clusters of galaxies would open up the possibility of further speculation about the arrangement of these various kinds of objects in sequences, and the chance of making up a scheme, relating these objects to one another, that has predictive power.

I hope that this in fact would be the case. It would be exceedingly interesting to evolve a scheme relating the unusual properties of these mysterious objects: the luminosity, which ranges from $10^{38}$ to $10^{47}$ ergs per second; the size, which may be smaller than a parsec; the spectrum shape for the continous radiation; the lifetime, which may be of the order of the million years; the number density of these things in the universe, which up to a red shift of order one seems to be about one per square degree; and the mass, which may range from about $10^{7}$ to $10^{13}$; solar masses.

Let me go even further afield than the astronomical example and make a few remarks about work in various behavioral sciences such as psychology, anthropology, sociology, and political science. Economics we place in a separate category which calls for a somewhat different treatment, but some of the remarks apply even there, in my opinion.

I would like to mention the fact that the making of schemes such as we have been discussing for the natural sciences is not very popular in the behavioral sciences either. It is not prestigious in our era to construct a phenomenological theory about a few simple quantities or a few simple facts arranged in a pattern, and make predictions based on this pattern. This is not the path of honor.

But perhaps it should be in some cases, because the alternatives are frequently unpleasant, One alternative is a trivialization of the subject matter. This occurs when one looks at a problem that has been so stripped of the complications which connect it to reality, so sanitized, that it is possible to quantify the facts very easily. A clean-looking theory is then constructed if possible using a good deal of mathematics. Such a treat-

ment can gain much credit, even though only the most cut-and-dried aspects of the subject have been treated. These aspects are not always the most exciting ones; the trivialization has often eliminated crucial qualitative considerations.

Furthermore, the search for easily analyzable parts of the subject at the expense of discussing the important ones presents a great danger in policy recommendations. For when the behavioral scientist gives advice to decision makers on matters of national concern, important values such as beauty, privacy, quality of life, justice, etc., which would have considerable effect on the decisions, may have been eliminated in favor of more easily quantifiable values. The decision makers may then proceed with some dehumanizing, mechanical plan that impoverishes our lives in some respects.

Of course, we understand that part of the drive toward quantification in the social sciences is merely a reaction to the loose talk and natural history which characterized these disciplines in previous centuries. Discarding the loose talk and woolly thinking is all to the good, but discarding the natural history approach, along with important qualitative features, seems to a me a mistake. It is perfectly possible to think carefully and logically about very soft subject matter.

Another unpleasant alternative to pattern-making is grandiose theorizing on an overambitious scale. This is the quality that we see in papers titled « Toward a General Theory of Society » and others of that kind. Here there is clearly a direct attempt to emulate Newton, but by « fiat » rather than by accomplishment. Unfortunately, many people seem to be drawn into this kind of work. It is as if they say to themselves, « What we need in this field is a Newton, and I will be that Newton »; it does not matter that it may be 200 years before one can use such a Newton — the temptation to become Newton immediately is irresistible.

Still another alternative is the trap of mere data-gathering. One can despair altogether of making a theory, and simply accumulate data without any attempt to establish correlations or patterns among them. One hopes for some other person to come along at a later time and arrange the facts in a useful form. A cure for this is to set more people to the work of modestly arranging the facts in patterns to find schemes with predictive power. Instead of this kind of effort, what seems to be on the rise is the construction of mathematical and computer models, again on a grandiose scale, and often having very little relation to the richness of the data and the richness of the ideas available in the relevant field.

An essential rule for successful scheme-making seems to be to match the amount of symbolism, the amount of computer work, and the amount of mathematics on the one hand with the scope of the data and the richness

of the concepts about the underlying subject matter on the other. Examples of the violation of this rule appear on all sides.

In many of the fields of study that we have discussed, it is a qualitative pattern or scheme that is important rather than one which is highly quantitative. This brings me to my final thought: Do we sufficiently encourage scheme-makers, particularly qualitative ones? Perhaps in our educational system we lay too little emphasis on natural history. Perhaps in our schools and universities and throughout the whole battery of intelligence and achievement tests that we use, we do not seek out enough persons with the talent to do the kind of work done by Mendeleev and Darwin and others of whom we have talked. This special talent requires an interest in patterns and a liking for natural history. We are speaking of people who love the facts in a particular field, who delight in arranging them, and who understand what constitutes a logical pattern, what constitutes predictive power, and what constitutes a test of a phenomenological theory.

I would like to encourage our society to search for such people, and to support them. I hope also, of course, that our new generation will produce Newtons for many of the subjects in science, but I think it is unlikely to happen right away in all of them.

D. V. SHIRKOV (*)

# The Puzzles of Elementary Particle Spectroscopy.

## 1.

During the last decade radical changes in our understanding of the elementary particles world has taken place.

To illustrate this progress I shall show you a table from Dr. C. N. Yang's book, « Elementary Particles » written in 1961 (fig. 1). This table contains 26 particles discovered experimentally (and 4 predicted theoretically) at that time. 19 of them are hadrons, particles participating in strong interactions and responsible for nuclear forces.

As a second illustration I should show you the last « Rosenfeld tables ». Instead of this I will only say that their baryon part (January 1969) contains 111 particles, and the meson part — 54 particles. Together with antibaryons we have 274 particles. Hence the wealth of contents of the elementary particle world is of the same order as that of Mendeleev's table of elements.

With some exclusions, all these particles are unstable and decay into the other ones. The well known example is the neutron, $\beta$ — decay — ing due to weak interactions (with a mean life time $\simeq$ 16 minutes). All hadrons of the Yang table except the proton are also unstable. Their decay- half-periods lie between $10^{-8}$ and $10^{-16}$ sec. These decays are due to weak and electromagnetic interactions.

However, with respect to strong interactions all these particles are stable ones. They now form just the first page of the « Rosenfeld tables », entitled « Stable particles ». The other two and a half hundred of hadrons have strong decays with a mean life time in the range of $10^{-22}$ — $10^{-24}$ sec. We also call them « resonances ». The first of them $\Delta_{33}$ ($M = 1236$, $IJ_P = 3/2\ 3/2^+$) was discovered in $\pi N$ scattering at the beginning of the fifties. This resonance with a mean life time of $5.10^{-24}$ sec decays into a pion and nucleon.

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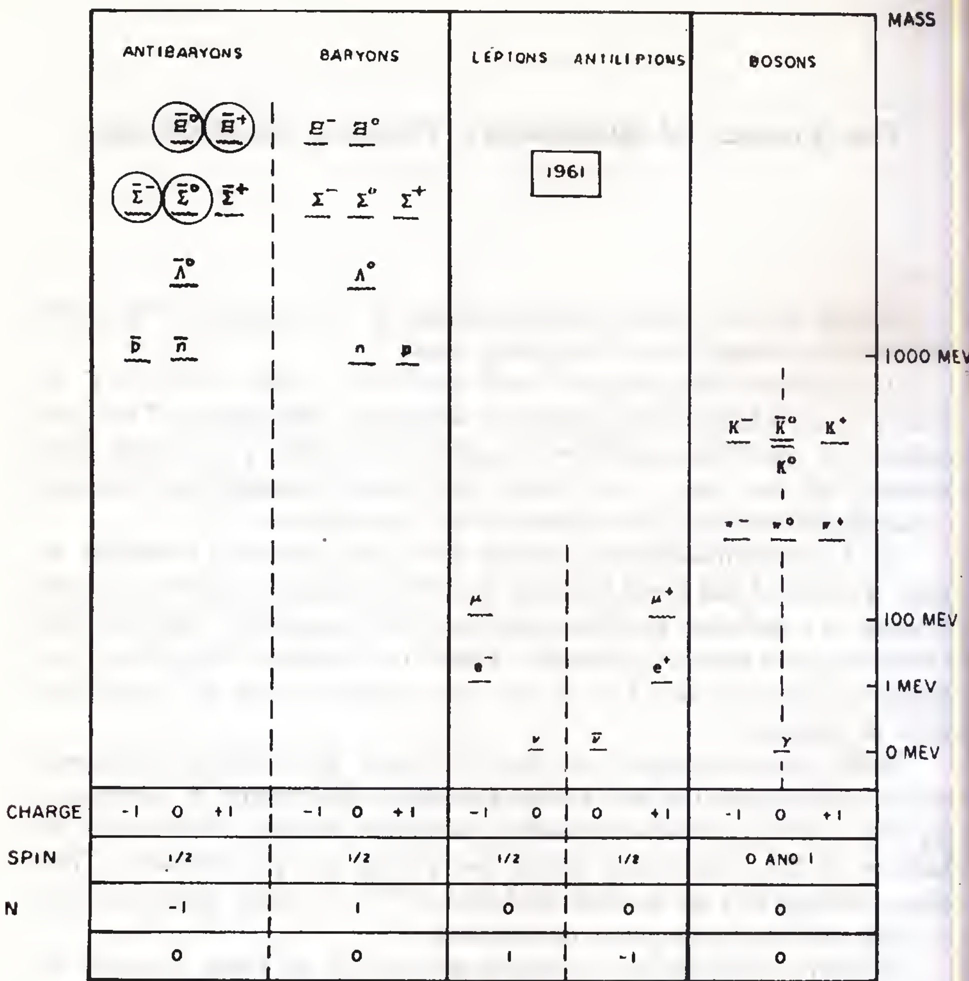
Nevertheless, it is absent in the Yang table. This is not a mistake. At that time it seemed natural to consider stable (with respect to strong interection) $\pi$, $K$ -mesons and $N$, $\Lambda$, $\Sigma$, $\Xi$ baryons to be primary (elemen-




*(Mass labeling schematic, not to scale.) Unstable particles are identified by wavy lines. Encircled particles are those theoretically predicted to exist but not yet experimentally found at this date.*

Fig. 1.

Yang's table of elementary particles (1961).

tary) particles, and resonances like $\Delta_{33}$, to be secondary entities composed of the primary ones like a deuteron is considered not to be an independent particle but a bound system of proton and neutron.

The first flaw in this philosophy was made by Fermi and Yang in the late forties. Fermi and Yang proposed to consider pions as bound states of nucleon and antinucleon.

After the discovery of strong mesons and baryons Sakata in 1956 proposed a model based on three basic particles: proton, neutron and $\Lambda$ -hyperon. In the Sakata model besides the pseudoscalar mesons ($J_P = 0^-$) formed by two « sakatons » with antiparallel spins, it is possible to obtain vector mesons ($1^-$), formed by two « sakatons » with parallel spins. Vector mesons $\varrho$, $\omega$, $K^*$, $\Phi$ were discovered experimentally at the beginning of the sixties. All of them are nuclear-unstable particles. It is essential here that the nuclear-stable particles (pseudoscalar mesons $0^-$) and resonances (vector mesons $1^-$) enter on an equal footing. The difference between stable (elementary) particles and unstable « resonances » then disappears.

A little bit later the second blow to « aristocratic hierarchy » of particles was delivered from another side. In 1962 Chew and Frautschi studying the concept of Regge poles, taken from nonrelativistic quantum mechanics, noticed that the stable and unstable particles entered this scheme in the same manner. The age of « aristocracy » was over. Its place was taken by « particle democracy ».

Particle democracy was effectively realized in a quark model of Gell-Mann and Zweig (1963). In the quark model not only mesons and meson resonances, but also baryon and baryon resonances are treated as bound states of hypothetical really « fundamental » particles — quarks and antiquarks.

At present the principal equality of stable hadrons and hadron resonances is universally recognized. Besides the achievments of the quark model, this is due to the success of the Regge pole model, a model which, during the last years, has taken a prominent position in the theory of strong interactions.

Below we consider hadron mass spectra from considerations of the quark model and the Regge pole positions.

## 2.

For describing baryonic mass spectrum a scheme of broken $SU(3)$ -symmetry turns out to be very fruitful. The $SU(3)$ group is a generalization of the isospin group $SU(2)$ and includes (as a group generator) a new quantum number — « strangeness » (or hypercharge $Y$), discovered in the late fifties. In the framework of this scheme (corresponding to a quark model) baryons and baryonic resonances form singlets ($\Lambda$), octets ($N$, $\Lambda$, $\Sigma$, $\Xi$) and decuplets ($\Delta$, $\Sigma$, $\Xi$, $\Omega$). In Table I you can see

the distribution of baryon resonances among $SU(3)$ multiplets. Here the superscript « ? » means unknown spin, and signs? « and ?? » in front of mass values correspond to uncertainty of the resonance existence. If we choose the presence of at least three resonances as a criterion for multiplet existence, then the « reliable multiplets » are $(8(1/2^+)$, $\underline{10}(3/2^+)$, $\underline{8}(3/2^-)$, $\underline{8}(5/2^-)$ and $\underline{8}(5/2^+)$. The degree of multiplet reliability is indicated in the second column. Table I includes 63 of 111 baryons from the « Rosenfeld tables » mentioned above.

TABLE I.

*Baryon multiplets.*

| SU(3) multiplets | Reliability | N*, Δ | Λ* | Σ* | Ξ* | Comments |
|---|---|---|---|---|---|---|
| 8(1/2⁺) | v | N(940) | Λ(1115) | Σ(1190) | Ξ(1320) | |
| 10(3/2⁺) | v | Δ(1236) | | (1382) | (1530) | Ω(1672) |
| 1(1/2⁻) | | | (1405) | | | Probably mixing |
| 8(1/2⁻) | | N(1550) | (1670) | ?(1650) | (1820)? | |
| 8(1/2⁻) | ? | N(1710) | ??(1750) | ?(1770) | (1820)? | |
| 1(3/2⁻) | | | (1520) | | | Mixing (— 16°) |
| 8(3/2⁻) | v | N(1520) | (1690) | (1660) | (1820)? | |
| 8(5/2⁻) | v | N(1680) | (1830) | (1765) | (1930)? | |
| 10(1/2⁻) | ? | Δ(1640) | | (1770) | | |
| 8(1/2⁺) | ? | N(1470) | ??(1745) | ?(1610) | (1820)? | |
| 8(5/2⁺) | v | N(1690) | (1815) | (1905) | (2030) | |
| 10(7/2⁺) | | Δ(1950) | | (2030) | | |
| 1(7/2⁻) | | | (2110) | | | |
| 8(7/2⁻) | ? | N(2190) | | (2250)? | | |

The mass splitting inside the baryon multiplets is usually described by a linear Gell-Mann-Okubo formula

$$\text{(GMO)} \qquad m = m_0 - \alpha Y + \beta \left\{ I(I+1) - \frac{Y^2}{4} \right\}.$$

Table II shows the central masses $m_0$, hypercharge splitting and isospin splitting intensities $\alpha$, $\beta$ for several multiplets from Table I. The

last column contains the errors of the mass formula (GMO), expressed in Mev. These errors [(except for $\underline{8}(5/2^+)$] are of the order of electromagnetic splittings and we may state that the accuracy of eq. (GMO) is excellent. This is well known from the brilliant story of $\Omega$-hyperon discovery.

TABLE II.

*The coefficients of linear formula GMO for baryon multiplets.*

| Multiplet | $m_0$ | $\alpha$ | $\beta$ | Accuracy | Comments |
|---|---|---|---|---|---|
| $\underline{8}(1/2^+)$ | 1112 | 190 | 39 | 3 | |
| $\underline{10}(3/2^+)$ | $m_0 + 2\beta = 1386$, | $\alpha - \frac{3}{2}\beta = 145$ | | 2 | $\beta$ taken from $\underline{8}(1/2^+)$ |
| | 1308 | 204 | (39) | | |
| $\underline{1}(3/2^-)$ | 1520 | — | — | | |
| $\underline{8}(3/2^-)$ | 1687 | 152 | − 12 | 3 | |
| $\underline{8}(5/2^-)$ | 1824 | 125 | − 30 | 4 | |
| $\underline{8}(5/2^+)$ | 1825 | 170 | 47 | 10 | |
| $\underline{10}(7/2^+)$ | $m_0 + 2\beta = 2030$, | $\alpha - \frac{3}{2}\beta = 80$ | | | $\beta$ taken from $\underline{8}(5/2^+)$ |
| | 1936 | 150 | (47) | | |

It is a priori unknown how to write the mass splitting formula: either in linear ($\sim m$) or in quadratic ($\sim m^2$) form. However, if instead of (GMO) we put

$$\text{(GMO}^2\text{)} \qquad m^2 = m_0^2 - \alpha' Y + \beta' \left\{ I(I+1) - \frac{Y^2}{4} \right\}$$

then the discrepancies will be several times higher. Thus the linear Gell-Mann-Okubo formula (GMO) describes the real mass splittings more accurately than quadratic one (GMO²).

However, using a somewhat different assumption on the structure of effects destroying $SU(3)$ symmetry it is possible (P. Bogoliubov, Matveev Struminsky), instead of (GMO), to obtain a rather different equation. Its quadratic version looks like

$$\text{(BMS}^2\text{)} \qquad M^2 = M_0^2 - aY + bI(I+1)\,.$$

The corresponding coefficients and errors are shown in Table III. Maximum mass errors $\delta M = \delta M^2/2M$ here do not exceed $\pm 2$ Mev, being

less than those for eq. (GMO). So we have no empirical choice between linear and quadratic mass scales.

TABLE III.

*The coefficients of quadratic BMS mass for baryon multiplets*

| Multiplets | $M_0^2$ | $a$ | $b$ | Accuracy | Comments |
|---|---|---|---|---|---|
| $\underline{8}(1/2^+)$ | 1,243 | 0,427 | 0,089 | 0,005 | |
| $\underline{10}(3/2^+)$ | 1,792 | 0,503 | 0,064 | 0,001 | |
| $\underline{1}(3/2^-)$ | 2,31 | | | | |
| $\underline{8}(3/2^-)$ | 2,86 | 0,51 | − 0,04 | 0,002 | |
| $\underline{8}(5/2^-)$ | 3,35 | 0,45 | − 0,11 | 0,002 | |
| $\underline{8}(5/2^+)$ | 3,32 | 0,63 | 0,18 | 0,008 | |
| $\underline{10}(7/2^+)$ | $M_0^2 + 2b = 4{,}12;\; a - \frac{7}{4}b = 0.36$ | | | | |
| | 3,76 | 0,67 | (0,18) | | $b$ taken from $\underline{8}(5/2^+)$ |
| | 3,82 | (0,63) | 0,15 | | $a$ taken from $\underline{8}(5/2^+)$ |

In fig. 2 the spectra of central masses $m_0$ and central mass-squares $M_0^2$ are plotted.

First, one can easily see that positive parity levels $\underline{8}(1/2^+)$ and $\underline{10}(3/2^+)$ are the lowest ones clearly separated from the others. They are followed by a big group of negative-parity levels, which in the upper part interesect the second group of positive levels. This structure has a simple explanation in the quark shell model.

In this model a baryon is considered to be a system of three tightly bound quarks. It is assumed that the elementary excitations of this system can be described by using a picture of three quasi-independent non-relativistic (quasi) quark, moving in the effective potential well. In the approximation of degeneracy with respect to $SU(3)$ quantum numbers (quark quantum numbers) and quark spins the states of a system can be described by a representation of the group $SU(6)$. This group joins the unitary spin group $SU(3)$ and the spin group $SU(2)$.

The ground state $(1s)^3$, in which every quasi-quark is in $(1s)$ state, corresponds to the 56-plet representation of $SU(6)$ with $L = 0$ orbital angular momentum and has a positive parity $P = +$. Due to spin unitary-spin interaction this $SU(6)$ supermultiplet splits into an $SU(3)$ decuplet $\underline{10}(3/2^+)$ and octet $\underline{8}(1/2^+)$. Just these levels in fig. 2 form the lowest group.

The second group of three quasi-particle states $(1s)^2(1p)$ [two quarks in $1s$ state, one quark in excited $1p$ state] corresponds to the $\underline{70}(L = 1)$

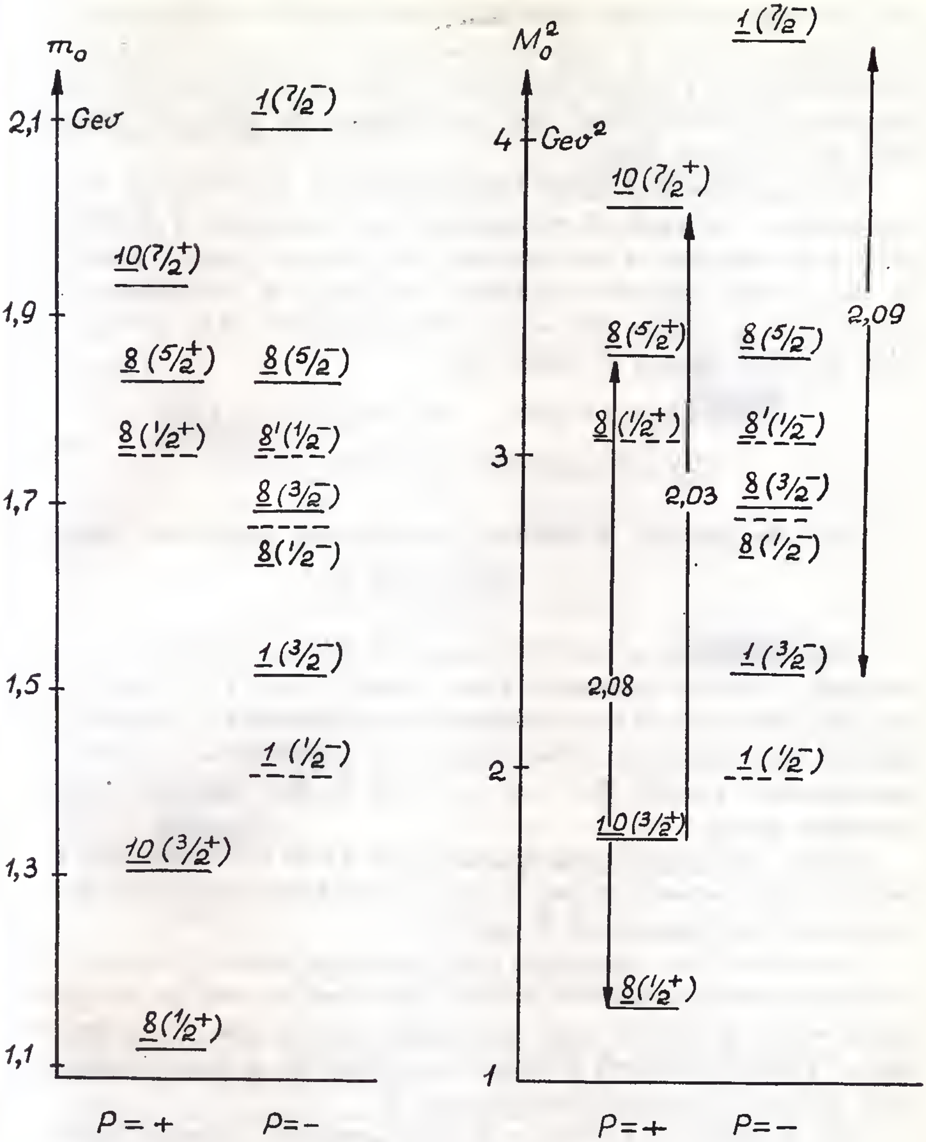



Fig. 2.
Baryon $SU(3)$ moltiplets mass spectra.

supermultiplet, consists of $\underline{70} \times (2L + 1) = 210$ negative parity particles and contains nine $SU(3)$ multiplets

$$\underline{70}(L = 1) = \underline{8}(5/2^-) + \underline{10}(3/2^-) + \underline{8}(3/2^-) + \underline{8}'(3/2^-) +$$
$$+ \underline{1}(3/2^-) + 10(1/2^-) + 8(1/2^-) + 8'(1/2^-) + \underline{1}(1/2^-)\,.$$

Here the well established multiplets from Table I are underlined with solid lines (__________). Underlined with dashed lines (— — —) are multiplets which are partially discovered. From fig. 2 we can see that the experiment confirms rather well the existence of $\underline{70}(L = 1)$ supermultiplet in the proper place.

The third group of states corresponds to $2s$ or $1d$ excited levels of one quark or $1p$ levels of two quarks. Here there arise 5 $SU(6)$-supermultiplets consisting of 816 particles with positive parity. From these we can partially see from experiment the $\overline{56}(L = 2)$ containing $\underline{10}(7/2^+)$ and $\underline{8}(5/2^+)$, as well as $\overline{56}(L = 0)$ containing $\underline{8}(1/2^+)$. The avarage mass levels for these groups of states are

$$M[(1s)^3] \simeq 1{,}2 \text{ Gev}, \qquad M[(1s)^2(1p)] \simeq 1{,}7 \text{ Gev}$$

$$M[(1s)^2(2s); (1s)^2(1d); (1s)\,(1p)^2] \gtrsim 2 \text{ Gev}\,.$$

Thus the energies of effective quasi-particle excitations are about

$$E(1p) - E(1s) \simeq 0{,}4 \text{ Gev}\,.$$

Now we proceed to the $SU(3)$ multiplet splitting which is due to the breaking of unitary symmetry. From Tables II and III it follows that the main effect here is the strangeness (or hypercharge $Y$) splitting. The value of this splitting in a linear mass scale (coefficient $\alpha$ in Table II) is approximately 140-180 Mev, i. e. 2-3 times smaller than the one-quark excitation energy.

Finally, the isospin mass splitting ($\beta$ in Table II) is again 3-4 times less and varies between 10 and 50 Mev. In the known multiplets, the sign of this splitting depends on $P$ -parity.

So we see that the baryon mass spectrum explicitly shows $SU(6)$ -symmetry which is however strongly disturbed, as well as $SU(3)$-symmetry which is broken more moderately, mainly due to hypercharge effects. This last property is usually associated (in a quark model) with mass increase of effective strange quark $\lambda$.

The fruitfulness of $SU(6)$ and $SU(3)$-symmetry schemes in baryon physics is also supported by the properties of strong and weak baryon decays, which however are completely out of the scope of our talk.

Let us proceed to mesons and mesonic resonances. Considering them to be bound states of quark + antiquark ($q\bar{q}$) we obtain a system of states with definite values of orbital angular momentum $L$, spin $S$ and total angular momentum $J = L,\ L - 1,\ L + 1$. The lowest $SU(3)$-multiplets (nonets) corresponding to $L = 0$ and $L = 1$ are drawn in fig. 3 in the mass scale. Black boxes represent experimentally discovered $0^{-+}$,

$1^{--}$, $2^{++}$ nonets. Shaded boxes correspond to partially observed $1^{-+}$, $0^{++}$ and $1^{++}$ nonets.

We shall not discuss the meson mass formulas, which are in general more complex compared to baryon ones. It is essential that they are quadratic and that the main effects can be described by attributing to the strange quark ($\lambda$) and antiquark ($\bar{\lambda}$) some additional mass.

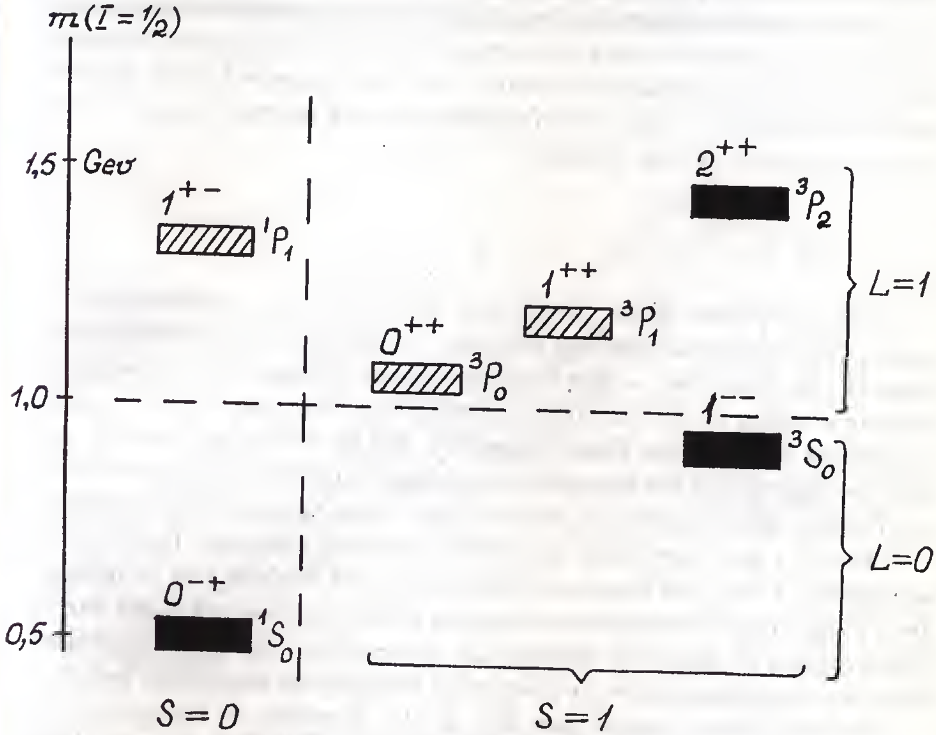



Fig. 3.
Meson $SU(3)$ multiplets mass spectra.

Fig. 3 gives an idea about mass spectra of meson multiplets which are very nicely located in the mass scale. Below 1 Gev we have states with zero orbital angular momentum $L = 0$. These states form $(0^{-+}, 1^{--})$ an $SU(6)$ 36-plet.

The $L = 1$ mesons occur between 1 and 1.5 GeV. The particles corresponding to $L \geq 2$ up to now have been discovered in small numbers, and we have no possibility of speaking of corresponding $SU(3)$ multiplets.

So we see that the quark model and $SU(6)$ symmetry explicitly correspond to the lower part of the mass spectrum.

The broken $SU(3)$ symmetry also can be seen in mass formulas (however, there exists some trouble, e. g. for $0^{++}$). Besides this, strong decays of $1^{--}$ and $2^{++}$ meson also support $SU(3)$ schemes.

The general important evidence in favour of $SU(6)$-symmetry (and also the quark model) is the absence of the so called « exotic » resonances, the resonances which do not enter the lower $SU(6)$ multiplets (and cannot be imagined as consisting of $q\bar{q}$ and $qqq$). Hence we can say that a hadron quark model gives a good quantitative description of regularities observed in hadron properties (among them the mass properties). This is a rather astonishing thing to the extent that we have no serious rationale for the nonrelativistic quark shell model, and we meet serious theoretical troubles (e. g. the problem of quark statistics connected with properties of the lowest baryon state) and furthermore have no good reasons to trust in the existence of free quarks.

## 3.

The fruitfulness of the Regge pole hypothesis in relativistic theory of strong interactions has become more and more obvious in recent years. At present the basic idea — the interdependence of a set of resonances with the same values of all quantum numbers except for spin values (t-channel resonances of the same Regge trajectory $\alpha(t)$ for $t > 0$), on the one hand, and the structure of the diffraction scattering pattern in the crossed s-channel (large $s$, small negative $t$), on the other hand, is universally recognized.

In fig. 4 the three most completely known trajectories ($\alpha_\varrho$, $\alpha_\delta$ and $\alpha_\gamma$) are drawn. From this figure one can see that all of them can be described by a linear (in $M^2$) expression within the known interval of $t = M^2$ variable (the property of *linearity*). Secondly, it is clear that the linear approximations for three trajectories are practically parallel (the *parallelism* property).

For the mass spectra (see fig. 2) the linearity of trajectories corresponds to equidistancy (in $M^2$ scale) between the set of mass levels, with the same quantum numbers differing only in 2 units of angular momentum (e. g. $\underline{10}(3/2^+)$, $\underline{10}(7/2^+)$, $\underline{10}(11/2^+)$, $\underline{10}(15/2^+)$, ...).

The parallel trajectories in their turn yield the equidistancy within the sets of different meson and baryon levels (see fig. 5).

At present we have evidence about the existence of at least three other meson, and four baryon, trajectories, They are experimentally known within the smaller $M^2$ variable interval.

However the data available do not contradict the linear structure with slopes equal to $0{,}9 \pm 0{,}1$.

Note also that the vertical shift between $\alpha_\delta$ and $\alpha_\gamma$ trajectories is close to 1. This property also seems to us not to be accidental.

Recently there have been theoretical speculations (Ademollo, Veneziano, Weinberg) on « quantization of vertical shifts » between « kindred »

parallel trajectories. The reasoning of this paper is rather complex. It employs the Veneziano model representation for the two-particle scattering amplitude as well as the so-called Adler consistency condition for scattering of a soft massless pion. The physically important idea here is the hypothesis about weakly broken chiral symmetry, corresponding to a neglect by pion mass. These authors came to the conclusion that the vertical distances between the trajectories connected by transition with

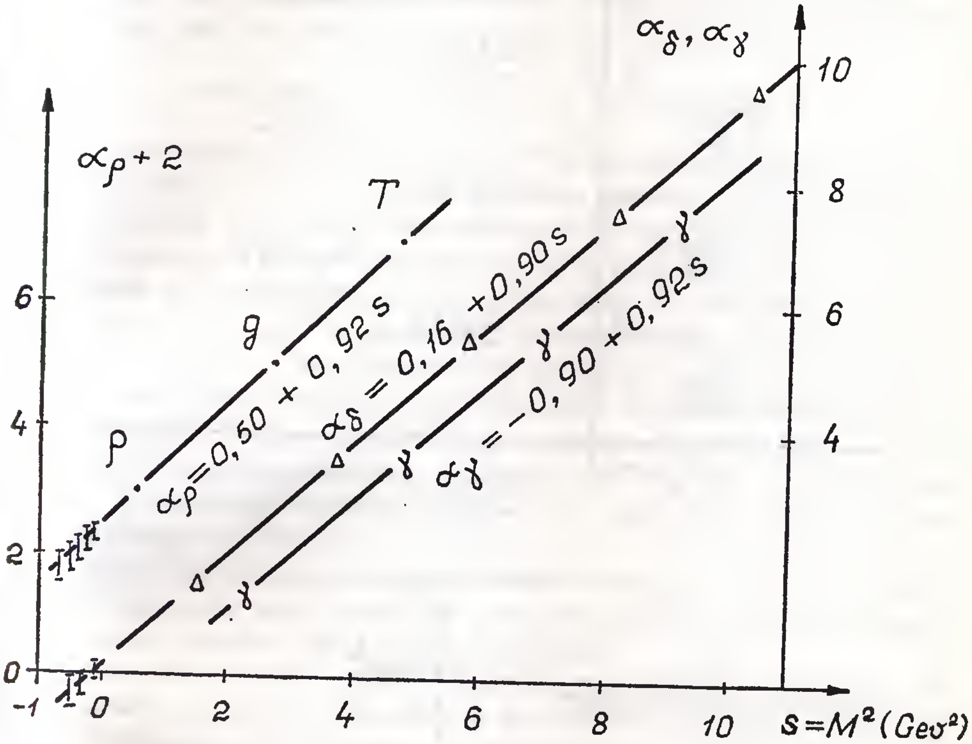



Fig. 4.
Linear approximation for $\alpha_\varrho$, $\alpha_\delta$, $\alpha_\gamma$ Regge trajectories.

pion emission had to be equal to 1/2. The corresponding shifts of squares of masses (for $\alpha' = 0.9$) must be equal to

$$\Delta m^2 = \frac{1}{2\alpha'} \simeq 0{,}55\ \text{Gev}^2 \simeq m_\varrho^2\,.$$

This rule of quantization for a number of cases is confirmed experimentally (see fig. 6).

It is essential that levels connected by transitions with pion emission always have different quantum numbers (besides angular momentum).

Fig. 5.
Mass-squared levels of nonstrange meson and baryon states.

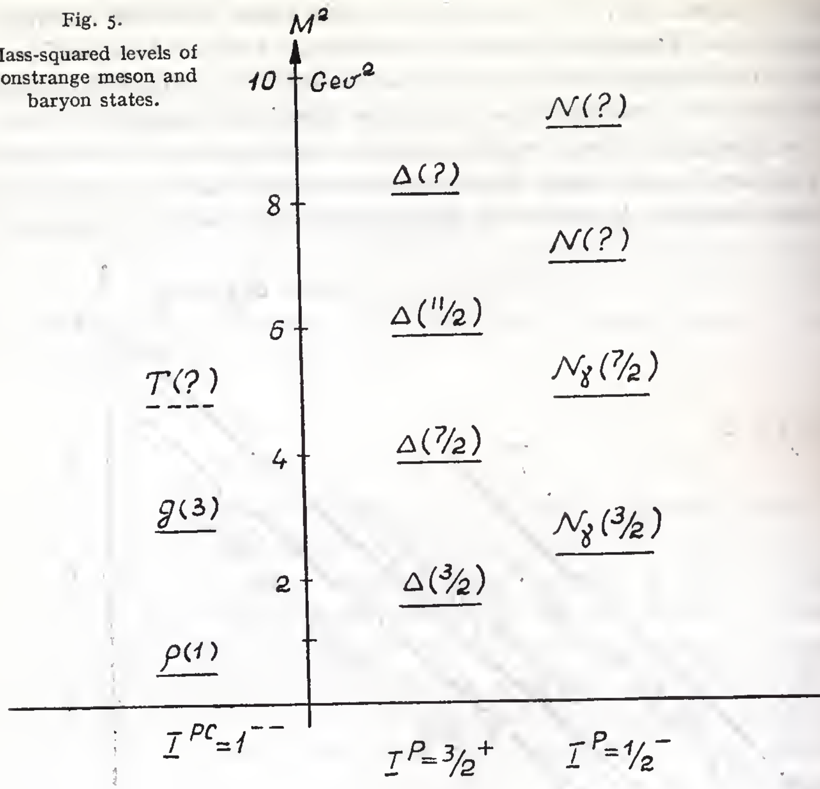
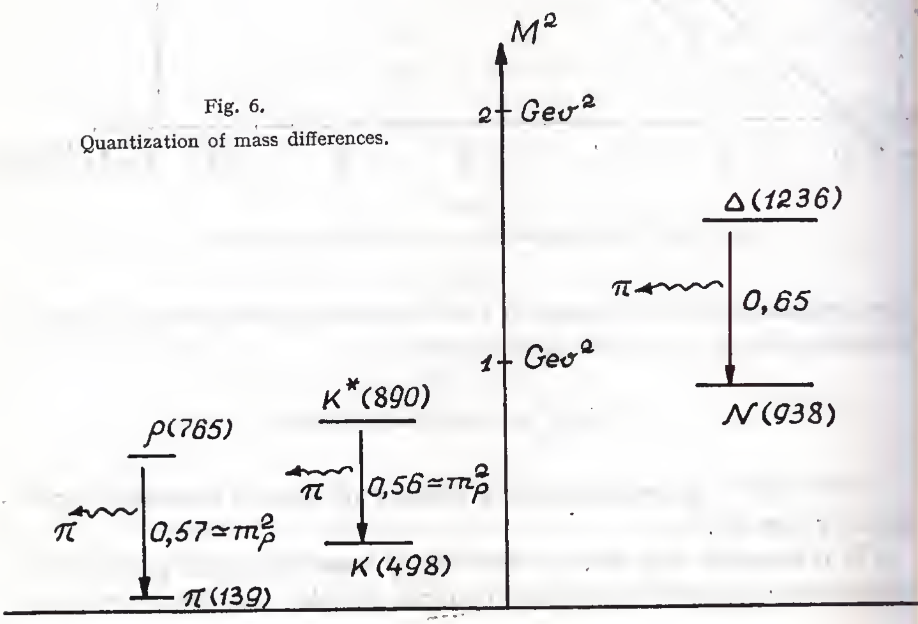



Fig. 6.
Quantization of mass differences.



So, the « shift quantization » leads to correlations between levels of different trajectories (with the same strangeness).

The most serious trouble with the Regge pole scheme at the moment seems to be a problem of « parity doubling » for baryon trajectories.

According to the existing formalism of introducing Regge poles into the scattering amplitude, each of the baryon trajectories turns out to be strongly related with its parity partner. Such a pair of trajectories $\alpha_+(t)$ and $\alpha_-(t)$ must coincide at $t = 0$. In the region of physical particle they can differ by the term proportional to $M = \sqrt{t}$

$$\alpha_\pm(t) = \alpha_0 \pm M\alpha_1 + M^2\alpha_2 = (\alpha_0 + \alpha_2 t) \pm \sqrt{t}\,\alpha_1 \quad (*)\,.$$

So the degree of deviation of $\alpha^+(M^2)$ from linear (in $M^2$) is a measure of the difference between it and its parity partner $\alpha^-(M^2)$. As we have seen from fig. 4, the linear approximations for nucleon $\alpha_\delta(I^P = 3/2^+)$ and $\alpha_\gamma(I^P = 1/2^-)$ trajectories are rather accurate ones. The term $\alpha_1$ in eq. (*) for these trajectories seems to be rather small. In the limit $\alpha_1 = 0$ the resonances with opposite parity must have the same masses (parity degeneracy). However, no sign of parity degenerate partners to resonances on $\alpha_\delta$ and $\alpha_\gamma$ have been seen experimentally. A curious situation occurs for the parity partner of $\alpha_\alpha(I^P = 1/2^+)$ nucleon trajectory [on which the nucleon $N$ (940) and resonance $N_\alpha$ (1690; $5/2^+$) lie]. For $N_\alpha$ (1690) there exists a practically degenerated partner $N_\beta$ (1680, $5/2^-$). However there is no partner for the nucleon at all.

One must note that in the framework of the baryon quark shell model the absence of a parity partner for the nucleon (as well as other parity degeneracy troubles) has a simple explanation.

However it is not simple to understand *linearity*, *parallelism* and *quantization* of Regge trajectories in the framework of quark model. Linearity evidently corresponds to oscillator-type spectrum, parallelism corresponds to equality of all $q\bar{q}$ and $qqq$ self-energies, and quantization corresponds to simple relations between the ground level positions.

« Why do the $q\bar{q}$ system have the same rotational frequencies as the $qqq$ has? » this is an example of questions, which arise here.

## 4.

Many, many years have passed from the time when the main goal of strong interaction theory was to explain nuclear foress, forces creating the atomic nuclei, to describe stable and unstable isotopes, to explain a nuclear basis of Mendeleev's periodical system.

In our days a central problem of strong interaction theory is an explanation of regularities of the world of resonances and particles, a world which is a very complex and multiform object.

The two above mentioned approaches in studying this object are really no more than formal semiphenomenological schemes. The first of them, using the idea of hypothetical fundamental particles (quarks) is more transparent from the physical point of view. Its main achievements are of qualitative character. Its formalism is nonrelativistic quantum mechanics + group theory.

37 years ago, when the proton-neutron nucleus model was formulated, the problem of nuclear theory was reduced to a problem of nuclear forces; in the quark model the problem of explanation of resonances and particles is reduced to interquark interaction. The situation repeats at another « level ».

The Regge pole model is more complicated from a theoretical point of view. It uses a concept of complex angular momentum, as well as a fundamental idea of relativistic field theory — the idea of crossing-symmetry, which has no analogue in nonrelativistic quantum mechanics. This model allows one to obtain a compact description of a large amount of regularities in particle mass spectra and (by use of crossing-symmetry) to relate them quantitatively with properties of particle scattering in the high energy region. However, in this approach there is no natural way to introduce dynamics.

The impression seems to be that the quark model and the Regge pole model in some sense are complementary and new progress of theory will be connected with their « interception ».

It is very probable that if, in the nearest future the free quarks are discovered experimentally, and the progress of theory leads to a mutual solution of their above-mentioned troubles, we shall get the complete theory of the world of resonances-particles. And that will be wonderful.

However let me express the hope that this will not be the case, that the solution of the problem will turn out not to be so simple from the *principal* point of view, and we shall not be able to put the final point to this story.

I mean that to get the answer we shall have to make more serious changes in our ideas, to make a step comparable with the creation of quantum mechanics. And this will be really wonderful.

Thank you for attention.

R. H. DALITZ (*)

# Parity, Charge Conjugation and Time Reversal.

## 1. Introduction.

One of the most remarkable chapters in the history of Science, and yet far from complete, has been the story of the change in our attitude to the role played in Physics by the symmetry operations associated with reflections of space and of time, and with reflections in the sign of charge.

For all of Man's time, it has generally been considered self-evident [1] that the *Laws of Physics* should not involve any preference for a particular «handedness» or «sense of helicity», that left-handed and right-handed systems of reference should stand on precisely the same footing as far as these laws are concerned, so that the form of these laws cannot be used as a means to distinguish left from right in an absolute way. This belief held despite the clear evidence of natural phenomena which showed a decided preference for one sense of helicity, such as the fact that many carbonic compounds with optical activity occur in Nature only with one sense for this optical activity; for example, the glucose which occurs in Nature has dextro-rotatory activity. However, it was shown that the preference for a definite helicity in Nature was not the result of any corresponding preference within the Laws of Atomic and Molecular Physics themselves. For example, laevo-rotatory glucose can be made in laboratory experiments and has the same stability as dextro-rotatory glucose. However, this laevo-rotatory glucose does not undergo the same chemical reactions with naturally occurring materials as does the naturally occurring dextro-rotatory form; on the other hand, the chemical reactions between two materials constructed to have opposite optical activity to that found for these materials in Nature do parallel exactly the reactions between the two materials in their naturally occurring forms. The sense of helicity in a molecule plays an important geometric role in the chemistry of that substance; a left-handed molecule may not fit into the same location with respect to a molecule with which it interacts as does the corresponding

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right-handed molecule, and may therefore fail to produce the same chemical reactions as induced by the latter, a situation with which the science of Stereo-chemistry is much concerned. The dominance of a particular helicity in naturally occurring organic material became understood as an evolutionary effect due to our environment, arising from the operation of chance in the very earliest stages of this evolution. The preference for a definite helicity in Nature was not due to any corresponding preference within the Laws of Physics and Chemistry, but resulted from a lack of symmetry in the boundary conditions (initial conditions, in the present case) subject to which these Laws have operated on our planet.

Similarly for time reversal, the phenomena in Nature show clearly an « arrow of time ». Natural systems develop according to a time sequence which is universal and unmistakable. We have no doubt about the direction of the flow of time, and it would be reasonable to expect this time-asymmetry in the world about us to be the consequence of some corresponding time-asymmetry in the basic Laws of Physics. Yet here again, we have learned that this is not necessarily the case, that this evidence does not imply any lack of invariance in the form of these basic laws with respect to reflection of the time axis. The evidence which has given us an « arrow of time » is interpreted to be a consequence of the laws of probability; the time development of a macroscopic system is understood as a progression from states of lesser probability for the system to states of greater probability, corresponding to an increasing entropy for the case of an isolated system. « Time's arrow » is thus given a sense by the direction of increasing entropy, by the direction of change in the state of the system towards configurations of greater statistical weight. Our daily experience of « time's arrow » has made us feel less committed to the belief that the basic Laws of Physics should be invariant in form with respect to reversal of the time axis. On the other hand, our past experience as physicists and chemists has shown us that time-reversal invariance of the basic Laws is quite compatible with everyday phenomena which appear contrary to this belief, and as sound scientists, conservative in our approach to new hypotheses which violate basic symmetry properties, we have naturally endeavoured to maintain this symmetry in the Laws put forward to account for new phenomena, as long as this was possible.

Today, we know that these symmetry properties are violated, space-reflection symmetry by the weak decay interactions, and time-reversal invariance by at least one still weaker sub-class of these decay interactions. Even so, we feel instinctively a deep reserve about the absolute distinction between left helicity and right helicity that the former of these violations appeared to imply. As said above, we feel less strongly about the failure

of time-reversal invariance, even though this failure turns out to have nothing to do with « time's arrow » as defined by macroscopic phenomena. However, as we shall discuss in a later chapter, the failure of time-reversal invariance carries with it a clear-cut empirical means to distinguish absolutely left from right, from the basic Laws of Physics themselves. Despite our deep reserve about such an absolute distinction between left and right, we must accept the evidence for it and learn to understand it.

## 2. Parity ($P$).

Under the reflection of space in a point (an operation we shall denote by $P$), the point being chosen to be the origin of our reference axes (held fixed), the position vector $\boldsymbol{r}$ and the momentum $\boldsymbol{p}$ of a particle are reversed, thus

$$P\colon\ \boldsymbol{r} \to -\boldsymbol{r}\,, \qquad \boldsymbol{p} \to -\boldsymbol{p}\,. \tag{2.1}$$

However, its angular momentum $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ then remains unchanged under this operation $P$; we distinguish such vector quantities as this by the name « axial vector », confining the term « vector » to quantities with the transformation (2.1). Its intrinsic spin $\boldsymbol{S}$ is also an angular momentum and must therefore be an axial vector like $\boldsymbol{L}$. Hence the helicity of a particle — its sense of spin about its direction of motion — reverses under the operation $P$, since the helicity is specified by the scalar product $\boldsymbol{S} \cdot \hat{\boldsymbol{p}}$, where $\hat{\boldsymbol{p}}$ denotes the unit vector $\boldsymbol{p}/|p|$.

The operation $P$ has the property that its operation twice brings the description of a system back to its initial description, that is $P^2 = I$. For a quantum-mechanical system, the eigenstates of the operator $P$ are limited to the eigenvalues $\pm 1$, but these eigenstates are appropriate to the description of physical systems only if the Hamiltonian is invariant under the operation $P$. The assumption that the laws of elementary particle physics are $P$-invariant thus requires that there should be assigned an *intrinsic parity* ($\pm 1$) for each particle in isolation. For example, the parity ($-1$) became established for the $\pi$-mesons, on the basis of the convention that the proton ($p$) and the neutron ($n$) have the same parity (a most reasonable convention since $p$ and $n$ are the two charge sub-states for the nucleon isodoublet), this latter parity being chosen to have the value ($+1$). Parity is also associated with the orbital motion of particles. For the motion of a particle with orbital angular momentum $L$ (unit $\hbar$, which takes the value unity in natural units), the parity is given by

$$P = (-1)^L\,. \tag{2.2}$$

For a system of particles, the energy eigestates may be classified in terms of the total parity, consisting of the product of the intrinsic parities for each of the particles and of the orbital parities $(-1)^L$ for each of the independent orbital motions within the system.

Our first inkling that $P$-invariance might not hold with complete generality came from the « $\tau$-$\theta$ puzzle ». For the two modes of $K^+$-meson decay,

$$\tau^+ \to \pi^+ + \pi^+ + \pi^- , \tag{2.3 a}$$

$$\theta^+ \to \pi^+ + \pi^0 , \tag{2.3 b}$$

it was established from a study of the pion-energy correlations in (2.3$a$) and from the decay angular correlations for both processes (2.3), that these processes lead to $s$-wave emission (i.e. emission with zero orbital angular momentum) for each of the pions. The same was also established for the corresponding $K^0$-meson decay mode

$$\theta^0 \to \pi^+ + \pi^- . \tag{2.4}$$

Yet this conclusion meant that the $3\pi$ state resulting from the $\tau$-mode of decay had *opposite parity* from that for the $2\pi$ state resulting from the $\theta$-mode of decay, since these states both have orbital parity $(+1)$, but intrinsic parities $(-1)^3$ and $(-1)^2$, respectively. The particle properties associated with the $\tau^+$ and $\theta^+$ modes of decay were measured in great detail — the masses, the lifetimes, the scattering cross-sections, and so on — but no other physical difference could be established between the particle with the $\tau^+$ decay mode and the particle with the $\theta^+$ decay mode. It became only possible to conclude that these two decay modes occurred from the same $K^+$ particle, leading to two final states which had opposite parity values, a situation which implied the failure of $P$-invariance for these decay interactions. However, this evidence was indirect and did not provide an explicit demonstration of $P$-violation.

In retrospect, it is curious that no one considered at that time the qualitative phenomenological connection between hyperon decay and the $K$-meson decay processes, through the sequence

$$\Lambda \to N + \overline{K} \to p + \pi^- . \tag{2.5}$$

The simplest possible graphs are depicted in Fig. 1, including the decay interactions $K^- \to \pi^+\pi^-\pi^-$ and $\overline{K}^0 \to \pi^+\pi^-$ which were well known at that time (the modes $\pi^-\pi^0\pi^0$ and $\pi^0\pi^0$ are now known to occur with rates about 1/4 and 1/2, respectively, of the corresponding charged modes, and the $K^- \to \pi^-\pi^0$ mode has been omitted since it is suppressed by the $\Delta I = 1/2$

rule for weak interactions and has a relatively small amplitude). The perturbative calculation necessarily leads to an amplitude for $\Lambda \rightarrow p\pi^-$ decay which takes the following form in the non-relativistic limit,

$$M(\Lambda \rightarrow p\pi^-) = s + p\boldsymbol{\sigma}_\Lambda \cdot \hat{\boldsymbol{q}}\,, \tag{2.6}$$

where $\hat{\boldsymbol{q}}$ denotes a unit vector along the outgoing pion momentum (seen in the $\Lambda$ rest frame) and the ratio $p/s$ is real. Although this calculation could not be reliable quantitatively, it would have been realised from

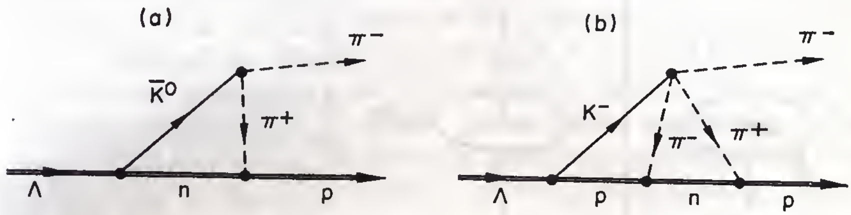


Fig. 1.

Feynman graphs showing the decay $\Lambda \rightarrow p\pi^-$ occurring in consequence of the interaction $\Lambda \rightarrow N\overline{K}$ and (*a*) the charged $\theta$-mode for $\overline{K}^0$ decay, and (*b*) the $\tau$-decay mode for $K^-$ decay.

this form (2.6) that the decay of polarized $\Lambda$ particles should then give an angular distribution with backward-forward asymmetry relative to the initial $\Lambda$-spin direction, of form

$$P(\hat{\boldsymbol{q}}) = (1 + \alpha\boldsymbol{\sigma}_\Lambda \cdot \hat{\boldsymbol{q}}) \tag{2.7}$$

where the asymmetry coefficient $\alpha$ is

$$\alpha = 2ps/(p^2 + s^2)\,. \tag{2.8}$$

It would then have been apparent that the observation of the pseudoscalar quantity $\alpha\boldsymbol{\sigma}_\Lambda \cdot \hat{\boldsymbol{q}}$ in this angular distribution could provide the kind of direct evidence needed to demonstrate explicitly the failure of $P$-invariance in the weak decay interactions.

A detailed perturbative calculation for the graphs of Fig. 1, assuming $\gamma_5$ coupling for the $K$-meson as for the $\pi$-meson (the latter assumed to interact strongly with nucleons only, for simplicity), leads to the following expression [2],

$$p/s = 0.4(f_3 q/f_2) G_{NN\pi} ln(1 + \Lambda^2/M^2)\,. \tag{2.9}$$

Here $f_2$ and $f_3$ denote the coupling constants for the decay processes (2.4) and (2.3*a*), respectively; the partial decay rates known correspond to the ratio $(f_3 m_K/f_2) \approx 1.5$. $G_{NN\pi}$ denotes the pion-nucleon coupling con-

stant in rationalized units (so that $G^2_{NN\pi}/4\pi \approx 14$), $q = 100$ MeV/$c$ is the magnitude of the decay pion c.m. momentum, $M$ denotes the nucleon mass, and $\Delta$ is a cut-off necessary for the evaluation of graph 1($b$). Taking $\Delta \approx M$ leads to the estimate $p/s \approx 1.6$, which corresponds to a value $\alpha \approx 0.9$. Although such perturbative calculations are not to be believed quantitatively, this estimate would have been encouraging as a qualitative indication that there was no reason to believe the asymmetry effects to be sought in $\Lambda \to p\pi^-$ decay should necessarily be negligibly small. It is interesting to remark that a search for this asymmetry in the decay of polarized $\Lambda$-particles produced in the $\pi^- p \to \Lambda K^0$ reaction could well have been carried out at that point in time (1956), just as it was in fact carried out several years later.

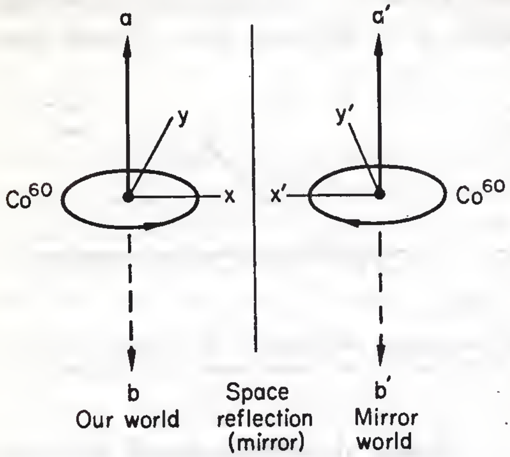


Fig. 2.

The figure on the left is a schematic representation of the beta-decay of completely polarized Co$^{60}$ nuclei, with their axes of spin along the direction $a$. The figure on the right shows the mirror reflection of these events; the reflected Co$^{60}$ nuclei are then completely polarized with opposite sense. An electron emitted in the direction $a$ appears as an electron emitted along $a'$ in the mirror-reflected world; a similar relationship holds for the directions $b$ and $b'$. More generally, an electron emitted upwards (downwards) relative to the plane of rotation of the Co$^{60}$ spin (upwards being defined by the right-hand rule with respect to the sense of the Co$^{60}$ spin) appears as an electron emitted downwards (upwards) relative to the plane of rotation of the Co$^{60}$ spin in the corresponding mirror-reflected world.

The actual path taken by history was that of Lee and Yang, who associated the question of $P$-failure with the totality of *weak interaction phenomena*, and who asked whether the assumption of $P$-invariance was directly tested by any of the phenomenology for beta decay processes. They came to the conclusion that there had been no experiments concerning the nuclear *beta-decay interactions* (the weak interaction process best known experimentally) which tested the property of $P$-invariance for them. This conclusion led directly to the celebrated experiment on the beta-decay of polarized Co$^{60}$ nuclei, carried out by C. S. Wu and the low temperature group at the National Bureau of Standards in Washington. This situation is depicted schematically in Fig. 2; the Co$^{60}$ nucleus is supposed completely polarized, with its spin pointing along the direction $a$. We then denote by $f_+$ the fraction of the electrons emitted in Co$^{60}$ beta-decay which are emitted into the upward hemisphere about this spin

axis $a$. Next, we consider these same events, as seen reflected in a mirror placed parallel to this axis. It is frequently more convenient for us to consider mirror reflection rather than the operation $P$ of reflection in a point. The two operations have equivalent consequences since mirror reflection corresponds to the operation $P$ followed by a rotation by angle $\pi$ about the normal to the mirror plane. The invariance of the Laws of Physics with respect to rotations has not been seriously doubted; it is equivalent to the law of conservation of angular momentum, a principle which has been tested rather rigorously [3] and which we shall assume here. In the mirror world, the sense of the $Co^{60}$ spin is reversed, so that the $Co^{60}$ polarization is now along the direction $b'$, and the events emitted into the hemisphere about $a$ are seen as events with electrons emitted into the hemisphere about $a'$. Hence, in the mirror world, the fraction of the electrons emitted in the decay of completely polarized $Co^{60}$ decay which are emitted into the hemisphere (about $a'$) downward with respect to the spin direction $b'$ is $f_+$, since these latter events are in one-to-one correspondence with the decay events seen in our world. If the Laws of Physics are $P$-invariant, and therefore have the same form in the mirror world as they do in our world, then we have to conclude, generally, that the fraction of electrons emitted into the downward hemisphere in the decay of completely polarized $Co^{60}$ is given by $f_+$. Since the upward and the downward fractions must sum to unity, we must conclude that $2f_+ = 1$, and that $P$-invariance for the Laws of Physics does not allow any up-down asymmetry relative to the spin polarization direction, in the process of beta-decay.

The observation of a large up-down asymmetry in the decay of polarized $Co^{60}$ nuclei therefore indicated that $P$-invariance was strongly violated in the process of nuclear beta-decay. In general, then, the laws of weak interaction physics are not $P$-invariant; this $P$-violation is not a small correction to them, but is comparable with a maximal violation of parity conservation. Such parity non-conservation effects have now been observed and measured for almost all of the weak decay processes accessible to us. This parity non-conservation will generally have observable effects also in the reaction processes induced by high-energy neutrinos, although none of these have yet been established for such reactions.

For the hadronic (strong, nuclear) and electromagnetic interactions, on the other hand, it has been found that parity conservation holds to a high degree of accuracy. In fact, the only $P$-violations which have been established to be significant [4] involve effects of order $10^{-5}$ (for example, in the detection of circular polarization for the $\gamma$-rays emitted from an unpolarized nucleus), and these effects can be satisfactorily attributed to the admixture of reversed-parity states to the nuclear states involved, with

amplitudes of order $10^{-6}$, which are due to strangeness-conserving weak interactions between nucleons. The existence of such $\Delta s = 0$ weak interactions was predicted by the weak-current hypothesis of Feynman and Gell-Mann [5], which gives the weak interaction a current-current form, since this form includes a term coupling the nucleon current weakly with itself.

### 3. Charge Conjugation (*C*).

The relation of particle with antiparticle is not directly connected with these space-time operations. However, this relation does stem from the *quadratic nature* of the basic invariant in special relativity, especially of the invariant $(E^2 - c^2p^2)$, and so the operation $C$, given by the replacement of every particle by its antiparticle,

$$C: \text{particle} \longleftrightarrow \text{antiparticle} \tag{3.1}$$

is intimately related with the space-time operations. Under the operation $C$, the charge $Q$ is reversed, as is also the baryon number $B$ (or the lepton number, as appropriate) and all other additive quantum numbers such as the strangeness $s$. However, the momentum and the spin of a particle are not affected by the operation $C$,

$$C: \mathbf{p} \to \mathbf{p}\,, \qquad \boldsymbol{\sigma} \to \boldsymbol{\sigma}\,, \tag{3.2}$$

and so there is no change in the helicity of the particle state under $C$.

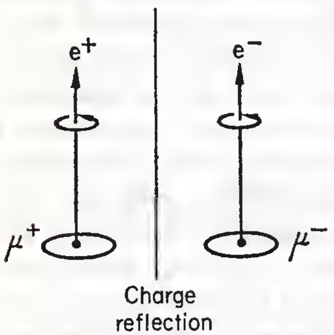


Fig. 3.

The figure on the left is a schematic representation of the process $\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu$ for unpolarized muons, showing the sense observed for the $e^+$ helicity. The figure on the right represents its charge reflection, the process $\mu^- \to e^- + \bar{\nu}_e + \nu_\mu$ for unpolarized muons, for which charge reflection leads to the same $e^-$ helicity. The experiments on $\mu^-$ decay indicate opposite $e^-$ helicity to that shown here, in clear contradiction to $C$-invariance.

The invariance of the physical interactions with respect to $C$ was expected to hold because of this intimate relationship between the properties of the particle and of the antiparticle. However, it has been demonstrated in an explicit way that $C$-invariance does not hold generally for the weak interactions. For example, we may consider the properties of the beta-decay of the muon,

$$\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu\,. \tag{3.3}$$

For unpolarized $\mu^+$ decay, the positrons emitted are known to have positive helicity (essentially 100%), as indicated on Fig. 3. If the laws of

beta-decay were invariant with respect to charge-conjugation $C$, then the corresponding property for $\mu^-$ decay would be obtained by carrying out this operation $C$ on the situation shown on the left of Fig. 3, leading to the following process, charge-conjugate to (3.3),

$$\mu^- \rightarrow e^- + \bar{\nu}_e + \nu_\mu . \tag{3.4}$$

Since the operation $C$ does not affect helicity, we would then be led to conclude that the electrons emitted from unpolarized $\mu^-$ decay should also have positive helicity. This conclusion is directly contradicted by the experimental observation of negative helicity (essentially 100%) for

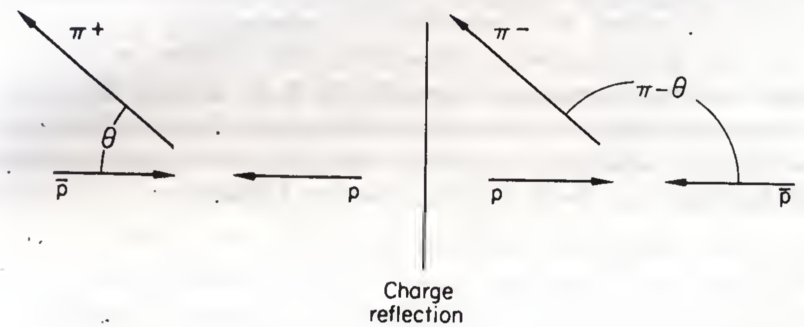


Fig. 4.

The figure on the left shows the emission of a $\pi^+$ meson at angle $\theta$ relative to the initial proton in a proton-antiproton collision (as seen in the c.m. system). The figure on the right is its charge reflection, and corresponds to the emission of a $\pi^-$ meson at angle $(\pi - \theta)$ relative to the initial proton in the c.m. system for a proton-antiproton collision.

these electrons. At least for the beta-decay interactions, the Laws of Physics are not the same in the charge-reflected world as in our world; these phenomena are not compatible with $C$-invariance.

The situation for the other classes of interaction is not so clear. Many predictions of $C$-invariance are difficult to test since they relate the properties of a reaction between particles with those for the corresponding reaction between the corresponding antiparticles, whereas the latter situation may be essentially impossible to achieve (e.g. we cannot readily measure the properties of $\pi^-$-antiproton scattering to compare them with the known $\pi^+$-proton data). The most convenient exceptions are those cases where the initial state can transform into itself under the operation $C$, for example the $\bar{p}p$ system or the neutral meson states. For the *strong interactions*, the most detailed test of $C$-invariance has been the comparison of the $\pi^+$ and $\pi^-$ angular distributions resulting from proton-antiproton collisions. The situation is illustrated in Fig. 4. Under the operation $C$, the production of a $\pi^+$ meson (together with any number

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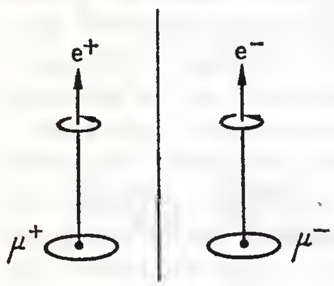


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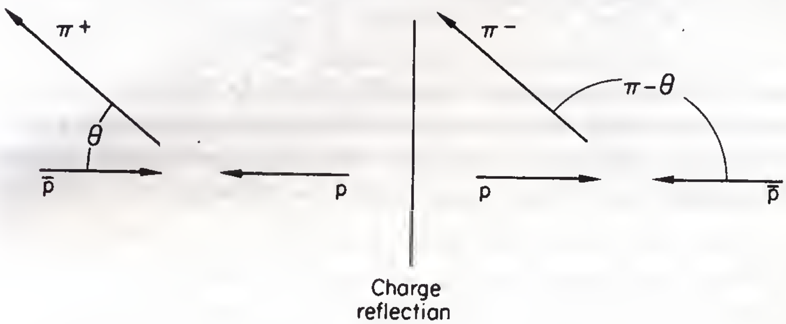


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of other particles) at angle $\theta$ relative to the ingoing proton direction is transformed into the production of a $\pi^-$ meson (together with the corresponding number of charge-conjugate particles) at angle $(\pi - \theta)$ relative to the ingoing proton. Hence, the assumption of $C$-invariance for the strong interactions leads to the prediction

$$\frac{d\sigma}{d\Omega}(\bar{p}p \to \pi^+, \theta) = \frac{d\sigma}{d\Omega}(\bar{p}p \to \pi^-, \pi - \theta)\,. \tag{3.5}$$

This prediction has been checked for many reaction processes, to an overall accuracy of better than 1%. There is a similar prediction relating the $K^+$ and $K^-$ angular distributions in $\bar{p}p$ interactions, and this has been satisfactorily checked, to a lower level of accuracy.

For the electromagnetic interactions, the validity of $C$-invariance has been seriously questioned, especially by T. D. Lee [6]. The violations of $C$-invariance which have been proposed are very large, with $C$-reversing interactions of magnitude comparable with the $C$-conserving interactions. The tests which have been carried out are as follows:

(*i*) the search for the decay mode $\eta \to \pi^0 e^+ e^-$. This process can occur with a rate proportional to $\alpha^2$ through $C$-violating electromagnetic interactions, whereas the $C$-conserving electromagnetic interactions only allow a rate proportional to $\alpha^4$. The observed $\eta$-decay processes are $\eta \to \gamma\gamma$ and $\eta \to 3\pi$, both of which have a rate proportional to $\alpha^2$. However, the one-photon transition $\eta \to \pi^0 + «\gamma»$, following which the electron pair is generated, is a $(0\,-) \to (0\,-)$ transition so that its amplitude is also severely restricted by the requirements of angular momentum and parity conservation, taken together with the requirements of gauge invariance. Further reasons for the suppression of this one-photon transition arise from the fact that the $\eta$ and $\pi^0$ mesons belong to the same unitary octet. In any case, this process has not yet been detected, the best upper limit being

$$\Gamma(\eta \to \pi^0 e^+ e^-)/\Gamma(\eta) < 1 \times 10^{-4} \tag{3.6}$$

(*ii*) charge asymmetry in the decay mode $\eta \to \pi^+\pi^-\pi^0$. This decay process occurs only through virtual electromagnetic interactions which allow the violation of isospin conservation necessary for the process. With $C$-violating electromagnetic interactions, an asymmetry between the $\pi^+$ and $\pi^-$ spectra can result from the interference between the $C$-violating and $C$-conserving transitions $\eta \to \pi^+\pi^-\pi^0$. Again, the $C$-violating amplitude will be suppressed by angular momentum barriers required by the constraints of angular momentum and parity conservation, for consistency with $C = -1$ for the final $3\pi$ state. There have been a number

of experiments, some reporting a small but significant asymmetry, others consistent with zero asymmetry. The most accurate experiment to date [7] has reported an asymmetry of $1.5 \pm 0.5\%$, and there are a number of more extensive experiments at present in preparation;

(*iii*) charge asymmetry in the decay mode $\eta \to \pi^+\pi^-\gamma$. The asymmetry would arise through interference between the amplitude for photon emission through the $C$-violating electromagnetic interaction and the normal amplitude for $C$-conserving photon emission. Again the $C$-violating amplitude is suppressed by angular momentum barriers, since it requires at least $d$-wave for the $\pi^+\pi^-$ system. No significant asymmetry has yet been detected, the best asymmetry coefficients reported to date being $2.4 \pm 1.4\%$ and $1.5 \pm 2.5\%$.

We must conclude that all of the evidence available on $C$-invariance for the strong and electromagnetic interactions is quite consistent with the absence of any $C$-violating interactions. At the same time, we must note that the tests which have been possible have not been particularly sensitive to the presence of $C$-violating interactions.

## 4. *CP* Invariance.

It was pointed out by Landau in 1957 that our intuitive unease about the absolute distinction between left and right resulting from the observation of $P$-violating effects could be satisfied by the hypothesis that all Laws of Physics were invariant under the combined operation of charge-conjugation $C$ and space-reflection $P$. In this situation, our $CP$-mirror reflection would change particle to antiparticle, as well as changing left helicity to right helicity. In place of Fig. 3, we would have Fig. 5; the $CP$-reflection of unpolarized $\mu^+ \to e^+$ decay would lead to a result in accordance with the experimental observation of the $e^-$ helicity for unpolarized $\mu^- \to e^-$ decay, so that this particular observation is in accord with the hypothesis of $CP$-invariance. However, Landau's remark was that we would then be able to use the basic Laws of Physics to distinguish left from right only if we were able to distinguish matter from antimatter in an *absolute* sense (i.e. from the Laws of Physics themselves and *not* by a contact comparison with some standard matter such as the matter about us on Earth).

To emphasize the point, let us consider the use of the $\mu \to e$ decay process as a means to communicate indirectly (i.e. not by direct contact) to a man in a far-off galaxy the definition of right helicity. If his galaxy were made of matter, then we could tell him to observe the helicity of

the light massive particle resulting from the $\mu \to e$ decay of unpolarized muons which had the same sign of charge as his nuclear charges. On the other hand, his galaxy might be made of antimatter so that his nuclear charges are negative, the elementary nuclear constituents being the antiproton and the antineutron. In that case, following our instructions, he would select $\mu^-$ mesons and observe the helicity of the electrons emitted from unpolarized $\mu^-$ decay. In this situation, our instructions would tell him to define this helicity as right helicity, which would actually be opposite to our definition of right helicity. We can give him instructions which will lead him to an empirical definition of right helicity in accordance with our usage *only if* we are able to know whether his galaxy is made of our matter or our antimatter. Apart from a comparison through direct contact, there is no way to settle this question; there is nothing in the Laws of Physics *at this stage of our discussion* which can allow him to determine by experiment whether he is made of our matter or our antimatter.

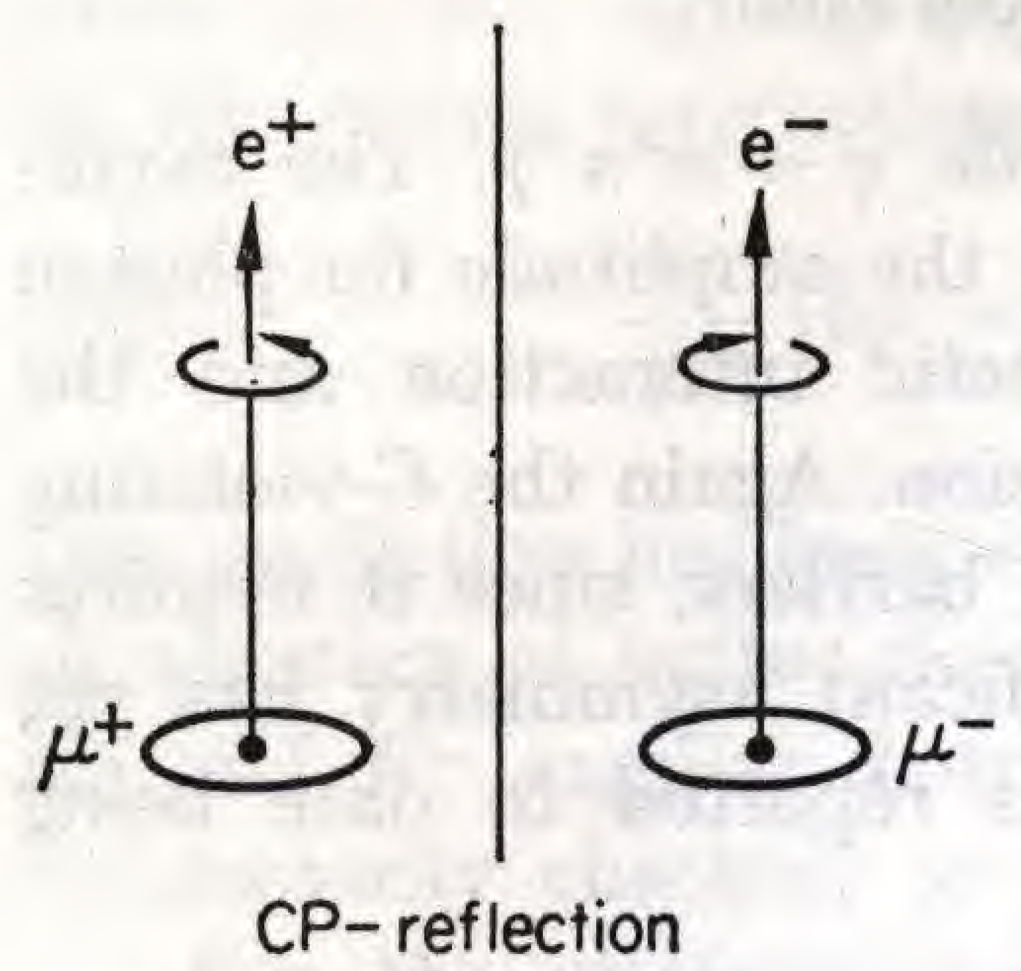


Fig. 5.
The figure on the left is a schematic representation of the process $\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu$ for unpolarized muons, showing the sense observed for the $e^+$ helicity. The figure on the right represents its $CP$-reflection, the process $\mu^- \to e^- + \bar{\nu}_e + \nu_\mu$ for unpolarized muons, leading to negative helicity for the electron, as is observed experimentally.

Thus, the hypothesis of $CP$-invariance for the Laws of Physics restored our previous philosophical position concerning the lack of any absolute distinction between left and right.

## 5. The Neutrino.

The most dramatic illustration of $P$- and $C$-violation is given by the case of the neutrinos $\nu_e$ and $\nu_\mu$. We know that only the neutrino states with left helicity ($\nu_{eL}$ and $\nu_{\mu L}$) participate in the weak interactions. For the antineutrinos $\bar{\nu}_e$ and $\bar{\nu}_\mu$, only the states with right helicity ($\bar{\nu}_{eR}$ and $\bar{\nu}_{\mu R}$) participate in the weak interactions. As far as the physics we know is concerned, the physics of the strong, electromagnetic and weak interactions, the other helicity state of the neutrinos ($\nu_{eR}$ and $\nu_{\mu R}$) and of the antineutrinos ($\bar{\nu}_{eL}$ and $\bar{\nu}_{\mu L}$) essentially do not exist; at least, they participate in none of these interactions (although they would presumably feel the very, very weak coupling of the gravitational field with their energy). This property of the neutrinos and the antineutrinos is exact only if they have exactly zero mass, as was pointed out by Salam [8].

The mass known for $\nu_e$ is now very low, the upper limit being 60 eV [9]; the upper limit for the mass of $\nu_\mu$ is at present 1.6 MeV.

For the physical neutrinos, then, the operation $P$ and $C$ lead to non-existing (or non-interacting) states,

$$P\nu_L = \nu_R\,, \tag{5.1 a}$$

$$C\nu_L = \bar{\nu}_L\,. \tag{5.1 b}$$

This is the most striking example of $P$- and $C$-violation. However, the operation $CP$ on the physical neutrino is satisfactory, since

$$CP\nu_L = \bar{\nu}_R\,, \tag{5.2}$$

leading to the physical state of the antineutrino.

On the other hand, to avoid misunderstanding, we should emphasize explicitly here that it is well known that these striking properties of the neutrinos are not the cause of the $P$- and $C$-violations observed. For example, as we have mentioned above, strong $P$- and $C$-violation effects are also observed in weak decay processes such as $\Lambda \to p\pi^-$ which do not involve leptons at all.

## 6. Time Reversal ($T$).

In classical mechanics, the equations of motion involve the time-derivative of the particle momentum and the time-independent potentials acting on and between the particles. The time-reversed motion simply corresponds to the replacements

$$T\colon\; t \to -t\,, \qquad \boldsymbol{p} \to -\boldsymbol{p} \tag{6.1}$$

for all the particles. The time-reversed motion is then compatible with the equations of motion, whose form remains invariant under $T$, and the motion corresponds precisely to the picture obtained by running the film of the original motion backwards.

In quantum mechanics, such a simple reversal of time is not really possible in practice. This is because a simple initial state (resulting from the interaction of two incident particles $a$, $b$, for example) develops in time to a coherent linear superposition of states, e.g.

$$\psi(a, b)_{\text{initial}} \xrightarrow{t} \sum_\alpha c_\alpha(t)\,\psi_\alpha(t) \tag{6.2}$$

where the suffix $\alpha$ refers to the constitution of the state (the number and type of particles in that state, their momenta and spin directions, for example). In order to reverse this time development, we would have to construct the time-reversed states $(\psi_\alpha)_T$ corresponding to each of the states $\psi_\alpha$ at some definite time $t_1$, and to superpose them with the correct amplitudes and phase relationships (corresponding with amplitudes $c_\alpha^*(t_1)$ at this time $t_1$). With this initial state, a Hamiltonian which is invariant in form with respect to the operation of time-reversal would then give a time-development leading ultimately to the state $T\psi(a, b)_{\text{initial}}$ describing two outgoing particles $a$, $b$ with their momenta and their spin directions opposite those for the initial state considered for the system $a$, $b$. However, although possible in principle, in practice we have no means to construct such a state, and so the useful consequences of time-reversal invariance in quantum mechanics take a rather different form from those in the classical case.

In quantum mechanics, the operator $T$ is not a unitary operator. Acting on a wavefunction $\psi$ describing a system of particles, it transforms $\psi$ to $\psi_T$, with the form

$$\psi_T = T\psi(\boldsymbol{p}_i, \boldsymbol{\sigma}_i) = \Lambda\psi^*(-\boldsymbol{p}_i, -\boldsymbol{\sigma}_i) \tag{6.3}$$

where $\Lambda$ is an operator with modulus unity acting on the spin spaces of the particles, and the asterisk denotes complex conjugation for any complex numbers which appear explicitly in the wavefunction $\psi$ (not including those in any representation of the basic spin states, nor in the differential operator representing momentum). It is termed an antilinear operator since

$$T(\Sigma_\alpha C_\alpha \psi_\alpha) = \Sigma_\alpha C_\alpha^* (\psi_\alpha)_T\,, \tag{6.4}$$

and it is frequently described as anti-unitary.

Hence, $T$-invariance for the interaction energy does not lead to any selection rules. Instead, it leads to relationships between matrix-elements. For the $S$-matrix, the canonical relationship is the statement of detailed balancing, the following equality between the $S$-matrix element for the reaction $a \to b$ and that for the reaction $b_T \to a_T$ between the time-reversed states,

$$(b\,|\,S\,|\,a) = (a_T\,|\,S\,|\,b_T)\,. \tag{6.5}$$

Under the operation of time-reversal, we have the following transformations for a given state (as stated already in Eq. (6.3), )

$$T\colon\ \boldsymbol{p} \to -\boldsymbol{p}\,, \qquad \boldsymbol{\sigma} \to -\boldsymbol{\sigma}\,. \tag{6.6}$$

More generally, for an operator $O$ and for states $a$, $b$, we have the relation

$$(b\,|\,O\,|\,a) = (b_T\,|\,O_T\,|\,a_T)^* , \tag{6.7a}$$

where $O_T$ denotes the operator obtained by the time-reversal of the operator $O$. If $O$ is invariant with respect to time-reversal, and if the states $a$, $b$ are bound states or stationary states (i.e. with standing waves at infinity for all the open channels), then the relation (6.7$a$) reduces to the reality statement,

$$(b\,|\,O\,|\,a) = (b\,|\,O\,|\,a)^* , \tag{6.7b}$$

for this matrix-element.

The tests of time-reversal invariance which have been carried out to date may be summarized as follows:

(*i*) *Strong interactions.* The most precise tests are those for detailed balancing in nuclear reactions, for example by comparison of the reaction rate for a given process and its inverse. Reactions which have been studied particularly precisely are [10, 11]

$$^{24}Mg + d \longleftrightarrow {}^{25}Mg + p , \tag{6.8a}$$

$$^{24}Mg + \alpha \longleftrightarrow {}^{27}Al + p , \tag{6.8b}$$

for which agreement has been found to an accuracy of better than 0.5%. Another test for the equality (6.5) is the comparison of the polarization $\mathcal{P}$ produced in $pp$ collisions with the asymmetry coefficient $\mathcal{A}$ in the angular distribution for the scattering of polarized protons by protons, since eq. (6.5) requires $\mathcal{P} = \mathcal{A}$. This equality has been tested by a number of experiments for protons with kinetic energy from 140 to 635 MeV, and the results have recently been summarized by Zulkarneyev et al. [12]. This test is rather less precise, of course; over all, we may say that the $T$-violating amplitude is not more than about 5% of the square root of the scattering intensity (we recall that a difference $(\mathcal{P} - \mathcal{A})$ will arise from the interference between this amplitude and the $T$-invariant amplitude).

(*ii*) *Electromagnetic interactions.* Tests of detailed balancing have recently been carried out by Bartlett et al. [13] and by Schrock et al. [14] for the reactions

$$n + p \longleftrightarrow d + \gamma . \tag{6.9}$$

It has been argued by Barshay [15] that no violations of detailed balancing are to be expected for these reactions until the incident neutron

reaches energies (about 450-650 MeV) appropriate to the excitation of $\Delta(1236)$. The experiments carried out to date are in general agreement with detailed balancing (individual points typically having accuracy $\pm 20\%$). However, it is interesting that the angular distribution data for neutron energies close to the resonance peak, in the range $580 \pm 60$ MeV for Bartlett et al. and $550 \pm 50$ MeV for Schrock et al., do happen to show a qualitative difference from the (far more accurate) data on the inverse photodisintegration reaction. Writing the angular distribution as $(A + B \cos \theta + C \cos^2 \theta)$, the value of $C/A$ is $-0.20 \pm 0.02$ in the photodisintegration experiments, whereas Bartlett et al. find $0.5 \pm 0.3$ and Schrock et al. find $+0.10 \pm 0.12$. These experiments are very difficult, but the discrepancy in the crucial energy range appears to be more than a three-standard deviation effect. Further and more accurate experiments in the $550 \pm 100$ MeV region will therefore be of great interest.

The searches for an electric dipole moment for the neutron and for the electron have been pushed to very great accuracy. However, its existence requires the failure of both $P$ and $T$. Since $P$-invariance holds very well for strong and electromagnetic interactions, the $P$-violation would have to be provided by the weak interactions, while the $T$-violation might arise through the electromagnetic interaction. This leads to a rough dimensional estimate for these electric dipole moments,

$$\mu_{e.d.} \approx eGM_P \approx 10^{-19} \text{ e.cm.} \tag{6.10}$$

The upper limits available at present are far beyond this estimate, as follows

$$\mu_{e.d.}(n) = (2 \pm 2) \times 10^{-23} \text{ e.cm.} \tag{6.11 a}$$

$$\mu_{e.d.}(e^-) < 5 \times 10^{-24} \text{ e.cm.} \tag{6.11 b}$$

These data provide a severe test for any theoretical model which asserts strong $T$-violation for the electromagnetc interactions.

(*iii*) *Weak interactions.* Here we shall not discuss any of the evidence concerned with the neutral $K$-meson complex, since this will be discussed separately in Chap. 8.

The tests which are available to date are the following reality tests:

(*a*) $n \to p + e^- + \bar{\nu}_e$. The phase of the ratio $G_A/G_V$ is now known to be very close to $180^\circ$. The most accurate value is that reported by Erozolimsky et al. [16], namely $(180 - (1.3 \pm 1.3))^\circ$.

(*b*) $\Lambda \to p + \pi^-$. Experiments [17, 18] on the proton polarization following polarized $\Lambda$ decay, measured perpendicular to the plane of the

$\Lambda$-polarization and the outgoing pion direction (both specified in the $\Lambda$ rest frame), have shown that the phase difference between the $s$-wave and $p$-wave decay amplitudes is only $2.8 \pm 4°$, after allowance for the small phase differences which result from the final-state pion-proton scattering.

(c) $K_{\mu 3}$ decay. The polarization of the final muon transverse to the plane of decay is given as $0.25 \pm 1.2\%$ by Young et al. [19]. The significance of this value depends on the structure of the $K_{\mu 3}$ amplitude, whose form is usually written

$$f_+(p_K + p_\pi)_\alpha + f_-(p_K - p_\pi)_\alpha \,. \tag{6.12}$$

With the best estimate $(-0.6 \pm 0.1)$ available for $Re(f_-/f_+)$, this known polarization leads to the limit

$$\mathrm{Arg}\,(f_-/f_+) = (1.5 \pm 7)° \,. \tag{6.13}$$

If $T$-invariance fails for the interaction energy, then the detailed balance equality (6.5) will fail for some processes. We should emphasize here that the failure of detailed balancing would not have any drastic consequences for thermodynamics. The important result, $\Delta S \geqq 0$, that entropy should always increase, does *not* depend on the validity of detailed balance. This was pointed out by Stuekelberg [20] some years ago, who demonstrated that the result $\Delta S \geqq 0$ can be proved assuming only *unitarity for the S-matrix*. In the equilibrium state, the lack of detailed balance between the reactions possible is made up by more complicated cycles of reactions. This possibility was already realised by Boltzmann in his derivation of the $H$-theorem for the classical case when he discussed the case of asymmetric molecules and gave some model illustrations of classical systems for which detailed balance would not hold [21].

## 7. The operation *CPT*.

The combination of the three reflection operations $P$, $C$, and $T$, discussed above has a special importance in view of the $CPT$ theorem which has been proved in great generality. For our purposes this theorem may be stated concisely as follows.

*CPT Theorem*: If a physical theory (lying within the framework of local relativistic field theory) is Lorentz-invariant under the continuous group of Lorentz transformations, then it is necessarily invariant with respect to the operation $CPT$.

The most concise proof of this theorem [22] depends on relating it to an equality between expectation values of the general form (expressed here for scalar fields),

$$(7.1)\quad (\mathrm{Vac}|\varphi(x_1)\varphi(x_2)\dots\varphi(x_n)|\mathrm{Vac}) = (\mathrm{Vac}|\varphi(-x_1)\,\varphi(-x_2)\dots\varphi(-x_n)|\mathrm{Vac}),$$

relating their values at a given set of space-time points $(x_1, x_2, \dots, x_n)$ and at their space-time inverses $(-x_1, -x_2, \dots, -x_n)$. The proof of this equality (7.1) rests on the fact that these vacuum expectation values are boundary functions of analytic functions and that this space-time inversion $x \to -x$ can be connected with the identity transformation $x \to x$ through complex Lorentz transformations.

For the $S$-matrix elements, this theorem has the consequence

$$(7.2)\qquad (b\,|\,S\,|\,a) = (a_{CPT}\,|\,S\,|\,b_{CPT})\,.$$

Under the operation $CPT$, we have

$$(7.3\,a)\qquad CPT\colon \text{particles} \longleftrightarrow \text{antiparticles}$$

$$(7.3\,b)\qquad \boldsymbol{p} \to \boldsymbol{p}\,, \qquad \boldsymbol{\sigma} \to -\boldsymbol{\sigma}\,.$$

Hence helicities are reversed under the operation $CPT$.

This $CPT$ invariance implies equalities between properties of particles and antiparticles. The outstanding tests available for $CPT$ are as follows:

(*a*) mass equalities. For $e^+$ and $e^-$, the masses are known to be equal to accuracy $10^{-5}$, which tests $CPT$ for electromagnetic interactions. For the charged $K$-mesons and pions, the particle-antiparticle mass equality is known to be satisfied to better than $10^{-3}$, which provides a test for the strong interactions. However, the mass equality best known is that for the neutral $K$-mesons. The mass difference $(m(\overline{K}{}^0) - m(K^0))$ cannot be measured directly but it is necessarily less than the measureable mass difference $(m(K_L^0) - m(K_S^0))$, which is now well known and leads to the limit

$$(7.4)\qquad \frac{m(\overline{K}{}^0) - m(K^0)}{m(K)} \leq \frac{m(K_L^0) - m(K_S^0)}{m(K)} = 0.71 \times 10^{-14}\,.$$

This is an exceedingly severe limit on $CPT$-violation for the strong interactions. It also provides the most severe limit available on $CPT$-violation for the electromagnetic interaction, of the order of $10^{-11}$, since the electromagnetic contributions to the neutral $K$-meson mass may be expected to be of the order $(\alpha/\pi)m(K)$. The result (7.4) even gives us the best upper limit for $CPT$-violation in the $\Delta s = 0$ weak interaction, of the order of $10^{-7}$.

(*b*) total lifetime equalities. Equality of the particle and antiparticle lifetimes are known typically to accuracy $0.5 \times 10^{-3}$, for $\mu^{\pm}$, $\pi^{\pm}$ and $K^{\pm}$ mesons.

(*c*) magnetic moment $g$-factor equalities. For the electron and muon, these $g$-factors are well known and provide a strong limit on $CPT$-violation for the electromagnetic interactions. For these particles the measured differences $\Delta g = (g(+) - g(-))$ are at present $\Delta g(\mu) = (-1.2 \pm \pm 1.6) \times 10^{-6}$ and $\Delta g(e) = (1.6 \pm 2.2) \times 10^{-5}$.

No violation of $CPT$-invariance is known (see also Chap. 8). The $CPT$ theorem is exceedingly deep and no field theory has been constructed to show in what way the theorem can be avoided. The only exceptions to this last remark are the infinite-component field theories discussed by Todorov [23]. Although these field theories are «local», their field equations necessarily involve an infinite number of derivatives, so that they may implicitly violate the condition of «locality» required in the general proof of the $CPT$ theorem. Further, Matthews and Feldman [24] have pointed out that such infinite-component field theories generally involve a number of rather unattractive features (e.g. the Spin-Statistics theorem is not necessarily valid) in comparison with the properties well-established for finite-component field theories.

## 8. The Neutral $K$-mesons and $CP$ Violation.

With $CP$-invariance for all interactions, the neutral $K$-meson complex $(K^0, \overline{K}^0)$ has two eigenstates, $K_{\pm}$ for the eigenvalues $CP = \pm 1$. These are related with the neutral $K$-meson states by the expressions

$$K_{+} = (K^0 + \overline{K}^0)/\sqrt{2}\,, \tag{8.1 a}$$

$$K_{-} = (K^0 - \overline{K}^0)/\sqrt{2}\,, \tag{8.1 b}$$

when the phase conventions have been arranged to give $CPK^0 = \overline{K}^0$. Since the neutral $\pi\pi$ state with $J = 0$ has $CP = +1$, the $\pi\pi$ decay mode is then allowed only for $K_{+}$; the $\pi\pi$ decay mode is forbidden for $K_{-}$, whose dominant decay modes are then of the forms $3\pi$, $\pi\mu\nu$ and $\pi e\nu$. This leads to the expectation that there should be a relatively short-lived neutral $K$-meson $(K_{+})$ with $2\pi$ decay, and a neutral $K$-meson $(K_{-})$ with much longer lifetime and three-particle decay modes. This is the situation observed empirically, the phenomenological description being that there are two neutral $K$-mesons, $K_S$ and $K_L$, $K_S$ having the shorter lifetime

$\tau_S = 0.86 \times 10^{-10}$ sec and $K_L$ having the longer lifetime $\tau_L = 5.4 \times \times 10^{-8}$ sec., the ratio of their total decay rates being $\tau_L/\tau_S \approx 630$.

In 1964, Christenson et al. [25] reported the observation of $2\pi$ decay for the long-lived neutral $K$-meson,

$$K_L^0 \to \pi^+ + \pi^- . \tag{8.2}$$

This represented a clear-cut violation of $CP$-invariance. The violation is certainly quite a small effect, relative to the general strength of the weak interactions, the branching ratio being $(1.57 \pm 0.04) \times 10^{-3}$ in $K_L^0$ decay. Its strength is conveniently specified by giving the ratio of amplitudes

$$|\eta_{+-}| = \left| \frac{A(K_L^0 \to \pi^+\pi^-)}{A(K_S^0 \to \pi^+\pi^-)} \right| = (1.90 \pm 0.05) \times 10^{-3} . \tag{8.3}$$

With $CPT$-invariance, this $CP$-violation would require $T$-violation for these weak interactions (see below); as we have discussed above, no $T$-violation effects have yet been established for any of the other weak interaction processes, despite considerable search.

Many experiments have now been carried out to confirm and extend these observation of Christenson et al. The empirical situation has been conveniently summarized by Steinberger [26]. The phase of $\eta_{+-}$ has been measured by two independent methods, which study the time-dependent interferences between the $K_L$ and $K_S$ amplitudes by observing the $\pi^+\pi^-$ intensity (*a*) following the passage of a $K_L^0$ beam through a regenerator, and (*b*) following a target at which $K^0$ mesons are produced. The two methods now give phase determinations in excellent agreement, the results being

$$\begin{aligned} \eta_{+-} &= A(K_L^0 \to \pi^+\pi^-)/A(K_S^0 \to \pi^+\pi^-) = \\ &= (1.90 \pm 0.05) \times 10^{-3} \times \exp i(40 \pm 6)^\circ . \end{aligned} \tag{8.4}$$

The neutral decay mode

$$K_L^0 \to \pi^0 + \pi^0 \tag{8.5}$$

has also become established by a number of experiments (cf. Table I), and a determination of the phase of its amplitude has been made by Chollet et al. [30]. All these data have been combined by Steinberger [26] to give the $2\pi^0$ amplitude ratio

$$\begin{aligned} \eta_{00} &= A(K_L^0 \to \pi^0\pi^0)/A(K_S^0 \to \pi^0\pi^0) = \\ &= (2.5 \pm 0.7) \times 10^{-3} \times \exp i(17 \pm 30)^\circ . \end{aligned} \tag{8.6}$$

However, this magnitude of $\eta_{00}$ has been determined by combining a number of experimental determinations whose consistency is not very satisfactory, and so we give the individual rates in Table I.

TABLE I.

*The values determined for* $|\eta_{00}|^2$ *by various experimental groups to date. They have been combined by Steinberger* [26] *to give the estimate* $|\eta_{00}|^2 = 6.3^{+4}_{-3} \times 10^{-6}$, *which corresponds to the value* (8.6) *for* $\eta_{00}$.

| Experimental group and reference | $\lvert\eta_{00}\rvert^2 \times 10^6$ |
|---|---|
| Princeton [26] | $-2 \pm 7$ |
| CERN-Orsay-Paris (H.L.B.C.) [28] | $5.05 \pm 1.9$ |
| Princeton [29] | $5.1 \pm 1.2$ |
| CERN [30] | $10.2 \pm 4.5$ |
| Aachen-CERN-RHEL [31] | $13 \pm 4$ |
| Berkeley-Hawaii [32] | $14.1 \pm 3.4$ |

One further $CP$-violation effect has been measured, the charge asymmetry for the lepton in the decay modes $K_L^0 \to \pi^- + l^+ + \nu$ and $\pi^+ + l^- + \bar{\nu}$. Two measurements have been reported for the $K_{e3}$ mode, and one measurement for the $K_{\mu 3}$ mode. The combined result from these experiments is [26],

(8.7) $$\delta_L = \frac{N_+ - N_-}{N_+ + N_-} = (2.7 \pm 0.3) \times 10^{-3}\,.$$

Two other physical parameters are of interest for the discussion of the neutral $K$-meson complex. The first is the mass difference between the $K_L$ and $K_S$ states. The value given in the 1969 compilation by Barash-Schmidt et al. [33] is

(8.8) $$(m_L - m_S)/\Gamma_S = 0.469 \pm 0.015\,,$$

where $\Gamma_S$ is the width corresponding to the $K_S$-meson lifetime $\tau_S = (0.862 \pm 0.006) \times 10^{-10}$ sec. There is also a recent determination of this mass difference by Rubbia et al. [34], $(m_L - m_S) = (0.542 \pm 0.005) \times 10^{10}\,\text{sec}^{-1}$, which leads to a further value for the ratio (8.8),

(8.9) $$(m_L - m_S)/\Gamma_S = 0.467 \pm 0.006\,.$$

The second parameter is the (charged)/(neutral) ratio for the decay $K_S \to \pi\pi$. The value given in the 1969 data compilation [33] is

(8.10) $$C = (\pi^+\pi^-)/(\pi^0\pi^0) = 2.16 \pm 0.14\,.$$

Since that time, two more accurate determinations have been reported,

$$C = 2.285 \pm 0.055 \text{ [35]},$$
$$C = 2.10 \pm 0.06 \text{ [36]}.$$

For the $(K^0, \overline{K}^0)$ system, $CP$-violation means that the mass matrix takes the following form [37],

$$\begin{pmatrix} M - \frac{i}{2}\Gamma & \beta \\ \beta' & \overline{M} - \frac{i}{2}\overline{\Gamma} \end{pmatrix}. \tag{8.11}$$

The eigenstates of this matrix correspond to the $K_S$ and $K_L$ mesons. These eigenstates may be written in the form

$$K_{S,L} = \{K^0(1 + \varepsilon_{S,L}) \pm \overline{K}^0(1 - \varepsilon_{S,L})\}/\{2(1 + |\varepsilon_{S,L}|^2)\}^{1/2}. \tag{8.12}$$

These two eigenstates are not generally orthogonal, their scalar product being given by

$$(K_S|K_L) = (\varepsilon_S^* + \varepsilon_L)/\{(1 + |\varepsilon_S|^2)(1 + |\varepsilon_L|^2)\}^{1/2}. \tag{8.13}$$

With the assumption $\Delta s = \Delta Q$ for the $K_{l3}$ interactions, the charge asymmetry (8.7) for the leptonic decay of $K_L^0$ is given by

$$\delta_L = \frac{|1 + \varepsilon_L|^2 - |1 - \varepsilon_L|^2}{|1 + \varepsilon_L|^2 + |1 - \varepsilon_L|^2} = \frac{2Re\varepsilon_L}{1 + |\varepsilon_L|^2}. \tag{8.14}$$

If $CPT$ invariance holds, then we have $\overline{M} = M$, $\overline{\Gamma} = \Gamma$, but generally $\beta \neq \beta'$. In this case $\varepsilon_S$ and $\varepsilon_L$ are equal, and we write

$$CPT\colon\ \varepsilon_S = \varepsilon_L = \varepsilon. \tag{8.15}$$

If $T$-invariance holds (since $CP$ is violated, this would imply $CPT$ violation and hence $\overline{M} \neq M$, $\overline{\Gamma} \neq \Gamma$, in general), then the mass matrix must be symmetric, so that we have $\beta' = \beta$ and the following equality,

$$T\colon\ \varepsilon_S = -\varepsilon_L = \overline{\varepsilon}. \tag{8.16}$$

In the approximation that only the $2\pi$ decay modes are considered (and the decay rate $\Gamma(K_S^0 \to \pi\pi)$ is certainly dominant over all the other decay rates by a factor of more than 300), then $\varepsilon$ necessarily has the phase $\varphi$, given by

$$\text{Arg}(\varepsilon) = \varphi = \text{artan}\{2(m_L - m_S)/(\Gamma_S + \Gamma_L)\} = 43°. \tag{8.17}$$

The phase of $\bar{\varepsilon}$ is then $\bar{\varphi}$, given by

$$\text{Arg}\,(\bar{\varepsilon}) = \bar{\varphi} = \varphi - \frac{\pi}{2}\,. \tag{8.18}$$

The $\pi\pi$ decay processes are then described by two amplitudes, corresponding to final states with $I = 0$ and $I = 2$. The amplitude for the transition to the $I = 0$ state from the $K^0$ state is defined by

$$K^0 \to (\pi\pi)_0\colon\ A_0 e^{i\delta_0} \tag{8.19}$$

where the phase convention for the states $K^0$ and $\bar{K}^0$ can be chosen so that $A_0$ is real, and $\delta_0$ denotes the phase-shift for $I = 0$ $s$-wave $\pi\pi$ scattering at the $K^0$ meson mass. In this case, the amplitude for $\bar{K}_0 \to (\pi\pi)_0$ is also given by expression (8.19). The amplitude for the $I = 2$ transition from the $K^0$ state is then written

$$K^0 \to (\pi\pi)_2\colon\ A_2 e^{i\delta_2}\,, \tag{8.20 a}$$

where $A_2$ is a complex number, in general, and $\delta_2$ denotes the phase-shift for $I = 2$ $s$-wave $\pi\pi$ scattering at the $K^0$ meson mass. The amplitude for the $I = 2$ transition from the $\bar{K}^0$ state is then given necessarily by the expression

$$\bar{K}^0 \to (\pi\pi)_2\colon\ A_2^* e^{i\delta_2}\,. \tag{8.20 b}$$

Then, with *CPT* invariance and the approximation that $\varepsilon$ and $A_2/A_0$ are small, the amplitude ratios $\eta_{+-}$ and $\eta_{00}$ which are of importance are given by the Wu-Yang expressions [37]

$$\eta_{+-} = \varepsilon + \varepsilon'\,, \tag{8.21 a}$$

$$\eta_{00} = \varepsilon - 2\varepsilon'\,, \tag{8.21 b}$$

where $\varepsilon'$ is given by the expression

$$\varepsilon' = \frac{i}{\sqrt{2}}\frac{ImA_2}{A_0}\exp i(\delta_2 - \delta_0)\,. \tag{8.22}$$

It is convenient to introduce also the quantity $\Delta$, given by

$$\Delta = \frac{i}{\sqrt{2}}\frac{ReA_2}{A_0}\exp i(\delta_2 - \delta_0)\,. \tag{8.23}$$

The (charged)/(neutral) ratio $C$ for $K_S^0$ decay is then given by

$$C = 2\,|(1 + \Delta)/(1 - 2\Delta)\,|^2\,, \tag{8.24}$$

apart from phase-space and electromagnetic corrections. The values quoted above for $C$ correspond to a value $|\Delta| \cos(\delta_0 - \delta_2) \approx 0.05$; for values of $(\delta_0 - \delta_2)$ now considered appropriate (see below), we have $|\Delta| \approx 0.07$, more than an order of magnitude larger than $|\varepsilon'|$. However, the role of $\Delta$ in the $CP$ violation phenomena is relatively minor and we shall generally neglect $\Delta$, for simplicity.

*T-invariance.* First, we shall consider the data under the assumption of $T$-invariance. With the approximations that $\bar{\varepsilon}$ and $A_2/A_0$ are small, the amplitude ratios are given by expressions analogous to eqs. (8.21),

$$\eta_{+-} = \bar{\varepsilon} + \bar{\varepsilon}', \tag{8.25a}$$

$$\eta_{00} = \bar{\varepsilon} - 2\bar{\varepsilon}' \tag{8.25b}$$

where $\bar{\varepsilon}' = i\varepsilon'$. There are two arguments which have been put forward.

(*i*) *The argument of Casella* [38]. This is based on the incompatibility of the ratio $r = |\eta_{00}|/|\eta_{+-}|$ with the value (8.4) known for $\eta_{+-}$, the phase $(-50 \pm 6°)$ known for $\bar{\varepsilon}$, and the phase of $\bar{\varepsilon}'$, which is given by the $\pi\pi$ phase-shift difference $(\delta_2 - \delta_0)$. The $\pi\pi$ phase-shifts are known only indirectly, of course, but there has been considerable clarification on this matter recently. Information about the small phase-shift $\delta_2$ ($\delta_2 = -8°$ at the $K$-meson mass) comes from the analysis of the reaction $\pi^+p \to n\pi^+\pi^+$ by Baton et al. [39]. A knowledge of the phase-shift $\delta_0$ has come from the study of the $s$-$p$ interference in the $\pi^+\pi^-$ c.m. angular distribution for the production reaction $\pi^-p \to n\pi^+\pi^-$, taken together with our knowledge of the $p$-wave $\pi^+\pi^-$ scattering associated with the $\varrho$-meson resonance. The Up-Down ambiguities of Malamud and Schlein [40] have been resolved by Morgan and Shaw [41] using a dispersion-theoretic analysis of $\pi\pi$ scattering, new $\pi\pi$ threshold data for the reactions $NN \to N\pi\pi$ obtained by Gutay et al. [42] and by Cline et al. [43], which lead to a value for the ratio $a_0/a_2$ of the $\pi\pi$ scattering lengths $a_I$, and the data available on the ratios $(\pi^0\pi^0)/(\pi^+\pi^+)$ and $(\pi^0\pi^0)/(\pi^+\pi^-)$ for these reactions, for $\pi\pi$ masses up to about 850 MeV. Morgan and Shaw concluded that the only solution which is consistent with the dispersion relations and which gives a good fit to these data is the Up-Down (or super-broad $\sigma$-meson) alternative. The solution depends on the $\sigma$-meson mass $M_\sigma$ assumed; the best fit corresponds to $M_\sigma \approx 900$ MeV, with the width $\Gamma_\sigma \approx 760$ MeV then determined by this choice. For the range of permissible choices for $M_\sigma$, they obtained values from 30° to 40° for $\delta_0$ at the $K$-meson mass, which lead to values between 40° and 50° for $(\delta_0 - \delta_2)$.

With these three phase angles for $\eta_{+-}$, $\bar{\varepsilon}$ and $\bar{\varepsilon}'$, and the triangular relation (8.25*a*), it will be found that $\bar{\varepsilon}$ and $\bar{\varepsilon}'$ must both be large relative to $\eta_{+-}$, which leads to the conclusion that $\eta_{00}$ must necessarily be very large relative to $\eta_{+-}$, which is contrary to the experimental ratio $r = 1.3 \pm 0.4$. Even for $(\delta_0 - \delta_2) = 0°$, the ratio $r$ cannot be less than 2.8 to close the triangle, whereas the largest of the individual values

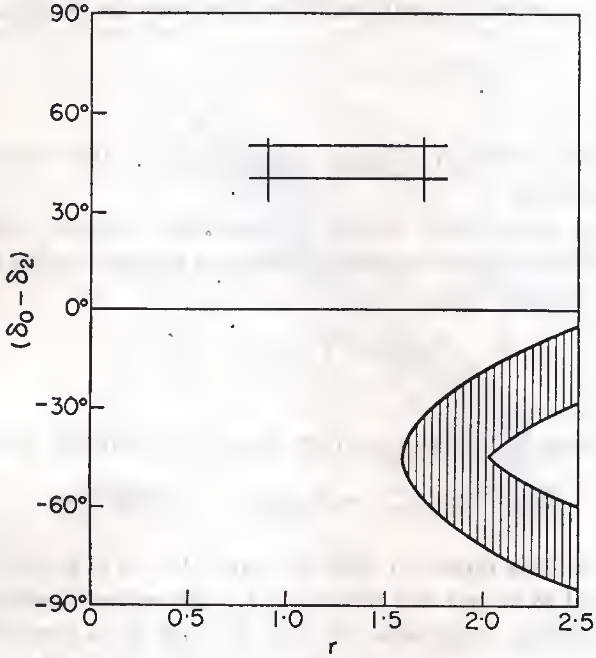


Fig. 6.

Diagram due to Casella [38], showing the region (shaded) for the variables $(\delta_0 - \delta_2)$ and $r = |\eta_{00}/\eta_{+-}|$ which allows a solution compatible with the magnitude and phase known for $\eta_{+-}$ and with the hypothesis of $T$-invariance. The empirical values $(\delta_0 - \delta_2) \approx (40° \text{ to } 50°)$ and $r = 2.5 \pm 0.7$ correspond to the small rectangle shown and lie well outside the allowed region, thus providing evidence against $T$-invariance for the $K_L \to 2\pi$ process.

reported for $|\eta_{00}|$ still gives only $r = 2.0$. The situation is shown as function of $r$ and $(\delta_0 - \delta_2)$ on Fig. 6; the shaded region indicates combinations of $r$ and $(\delta_0 - \delta_2)$ for which the data are compatible with eqs. (8.25), and the rectangle outlined shows the range allowed empirically.

(*ii*) *The unitarity relation*, given by Bell and Steinberger [44], takes the form

$$\left\{ \frac{\Gamma_S + \Gamma_L}{2\Gamma_S} + i\,\frac{m_L - m_S}{\Gamma_S} \right\} (K_S \mid K_L) = \sum B_f \eta_f\,, \tag{8.26}$$

where $B_f$ and $\eta_f$ denote the following ratios

$$B_f = \Gamma(K_S \to f)/\Gamma(K_S) \,, \tag{8.27}$$

$$\eta_f = (f\,|\,S\,|\,K_L)/(f\,|\,S\,|\,K_S) \,, \tag{8.28}$$

for the final state $f$, and the sum in eq. (8.26) is to be taken over all the final states energetically available. The sum may be written

$$\sum_f B_f \eta_f = B_{+-}\eta_{+-} + B_{00}\eta_{00} + \gamma \,, \tag{8.29}$$

where $\gamma$ denotes the sum $(\Sigma_f' B_f \eta_f)$ taken over all the final states other than the $2\pi$ states.

From eqs. (8.13) and (8.16), $T$-invariance requires that $(K_S|K_L)$ should be a pure imaginary number. Hence, as pointed out by Gourdin [45], $T$-invariance requires that

$$Re(e^{-i\varphi} \sum_f B_f \eta_f) = 0 \,, \tag{8.30}$$

where $\varphi$ is given by eq. (8.17). This may be re-written conveniently as

$$Re\{e^{-i\varphi}(B_{+-}\eta_{+-} + B_{00}\eta_{00})\} = -\,Re(e^{-i\varphi}\gamma) \,. \tag{8.31}$$

The left side of this equation has the value $(2.0 \pm 0.4) \times 10^{-3}$ using the values (8.3) and (8.6) and the values for $C$. The experimental upper limits on the $CP$-violating amplitudes for the $K_{l3}$ and $K \to \pi^+\pi^-\pi^0$ modes give an upper limit of $2.9 \times 10^{-4}$ for the right side of eq. (8.31). This upper limit omits the final state $3\pi^0$ since very little is known about the mode $K_S^0 \to 3\pi^0$. However, the $3\pi^0$ contribution to $\gamma$ may be written

$$\begin{aligned} &|\eta_{3\pi^0}|^{-1} \cdot \Gamma(K_L \to 3\pi^0)/\Gamma_S = \\ &= (3.5 \pm 0.2) \times 10^{-4}\,|\,(3\pi^0\,|\,S\,|\,K_S)/(3\pi^0\,|\,S\,|\,K_L)\,| \,. \end{aligned} \tag{8.32}$$

We expect the $CP$-violating amplitude $(3\pi^0\,|\,S\,|\,K_S)$ to be small relative to the $CP$-conserving amplitude $(3\pi^0|S|K_L)$. Even if the two amplitudes were equal, there would still be a significant discrepancy between the left and right sides of (8.31); Kabir [46] has estimated an upper limit of $4.9 \times$ $\times\, 10^{-4}$ for the latter.

Ashkin and Kabir [47] have suggested a convenient way to plot this relationship, shown on Fig. 7. The shaded area shows the region to which $(B_{+-}\eta_{+-} + B_{00}\eta_{00})$ is confined by the relation (8.31), where $R_T$ denotes the upper limit given by Kabir [46] for its right-hand side. The value of

$\eta_{+-}$ is well known; for any point $Z$ lying within the shaded strip, the corresponding value required for $\eta_{00}$ is then given by

$$\eta_{00} = Z/B_{00} - \eta_{+-}/C \tag{8.33}$$

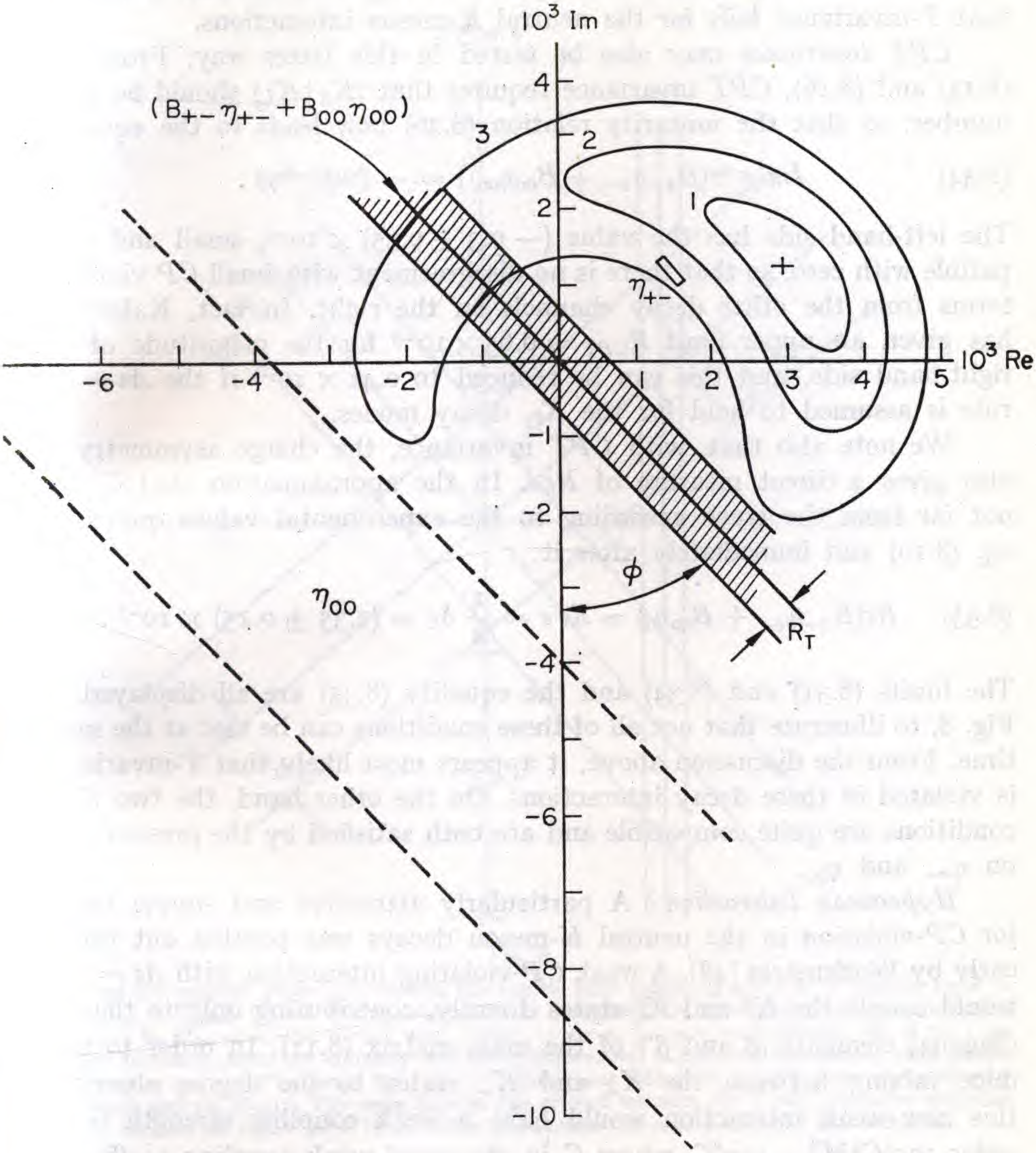


Fig. 7.

A plot of the complex plane, showing the $CP$-violation parameter $\eta_{+-}$, the narrow strip ($\pm R_T = \pm 4.9 \times 10^{-4}$) allowed by $T$-invariance [46] for the sum $Z = (B_{+-}\eta_{+-} + B_{00}\eta_{00})$ where $B_f$ denotes the branching ratio for the final state $f$ in $K_S$ decay, and the broad strip then allowed by $Z$ and $\eta_{+-}$ for the $CP$-violation amplitude $\eta_{00}$. The cross marks the empirical value (8.6) for $\eta_{00}$ and the $\chi^2$ contour lines shown are taken from refs. [30, 47]. The curves labelled $N$ include all the $\eta_{00}$ parameter values within $N$ standard deviations from the best fit.

and must lie in the strip enclosed by the dashed lines. We note that this relationship excludes the first quadrant for $\eta_{00}$, and requires that a negative phase for $\eta_{00}$ should lie below $-50°$, contrary to the experimental data at present.

These two arguments make a very strong case for the conclusion that $T$-invariance fails for the neutral $K$-meson interactions.

*CPT invariance* may also be tested in this latter way. From eqs. (8.13) and (8.16), $CPT$ invariance requires that $(K_S | K_L)$ should be a real number, so that the unitarity relation (8.26) now leads to the equation

$$(8.34) \qquad Im\{e^{-i\varphi}(B_{+-}\eta_{+-} + B_{00}\eta_{00})\} = -Im(e^{-i\varphi}\gamma) \,.$$

The left-hand side has the value $(-0.3 \pm 0.35) \times 10^{-3}$, small and compatible with zero, so that there is no disagreement with small $CP$-violating terms from the other decay channels on the right. In fact, Kabir [46] has given an upper limit $R_{CPT} = 0.65 \times 10^{-3}$ for the magnitude of the right-hand side, and this can be reduced to $0.41 \times 10^{-3}$ if the $\Delta s = \Delta Q$ rule is assumed to hold for the $K_{l3}$ decay modes.

We note also that, with $CPT$ invariance, the charge asymmetry $\delta_L$ also gives a direct measure of $Re\,\varepsilon$. In the approximation that $C = 2$, not far from the truth according to the experimental values quoted in eq. (8.10) and immediately after it,

$$(8.35) \qquad Re(B_{+-}\eta_{+-} + B_{00}\eta_0) \approx Re\,\varepsilon = \frac{1}{2}\,\delta_L = (1.35 \pm 0.15) \times 10^{-3} \,.$$

The limits (8.31) and (8.34) and the equality (8.35) are all displayed on Fig. 8, to illustrate that not all of these conditions can be met at the same time. From the discussion above, it appears most likely that $T$-invariance is violated in these decay interactions. On the other hand, the two $CPT$ conditions are quite compatible and are both satisfied by the present data on $\eta_{+-}$ and $\eta_{00}$.

*Hyperweak Interaction?* A particularly attractive and simple model for $CP$-violation in the neutral $K$-meson decays was pointed out rather early by Wolfenstein [48]. A weak $CP$-violating interaction with $\Delta s = \pm 2$ would couple the $K^0$ and $\bar{K}^0$ states directly, contributing only to the off-diagonal elements ($\beta$ and $\beta'$) of the mass matrix (8.11). In order to produce mixing between the $K_+$ and $K_-$ states to the degree observed, this new weak interaction would have a weak coupling strength $G_2$ of order $10^{-3}G^2M_P^2 \approx 10^{-8}G$, where $G$ in the usual weak coupling coefficient $G \approx 10^{-5}/M_P^2$, since its characteristic matrix-element must be about $10^{-3}$ times the $K_S$ lifetime width, the latter being a quantity of second order in the usual weak coupling. Hence it is convenient to refer to these very weak interactions as *hyperweak*. The observed decay processes then occur through the usual $CP$-conserving weak interactions of strength $G$;

thus the $CP$-violating decay $K_L^0 \to \pi\pi$ occurs through the normal decay interaction $K_+ \to \pi\pi$ in virtue of the small admixture of $K_+$ state in the $K_L$ state, induced by the $CP$-violating hyperweak interaction. The $CP$-violating decay processes would then be described by one complex parameter, the amplitude $\varepsilon$.

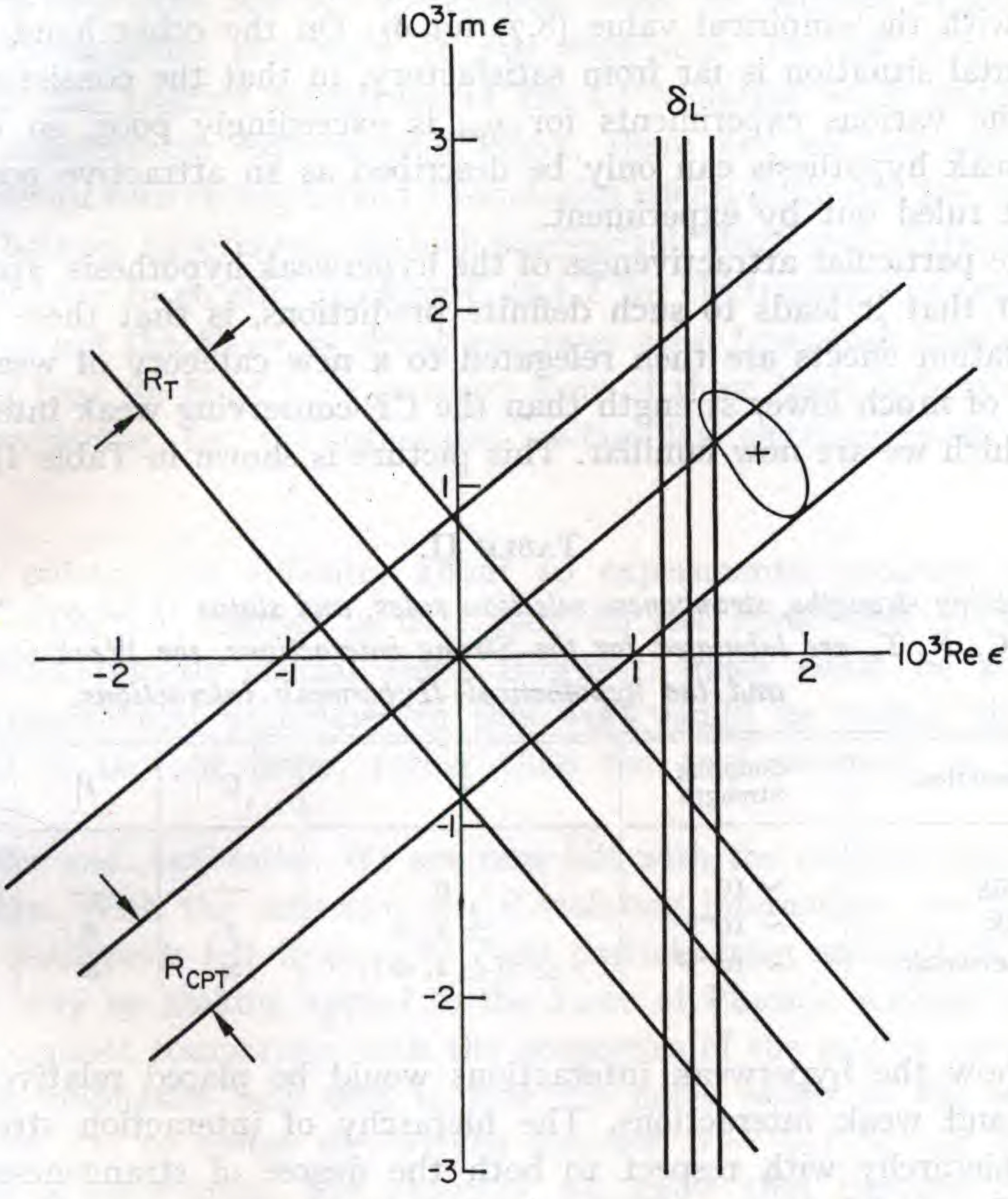


Fig. 8.

A plot of the complex plane [46] showing the narrow strip (width $\pm$ 1.7 $\times$ 10$^{-4}$) allowed for $Z = (B_{+-}\eta_{+-} + B_{00}\eta_{00})$ by the lepton asymmetry $\delta_L$ (assuming $CPT$-invariance and the branching ratio $C = B_{+-}/B_{00} = 2$), the narrow strip (width $\pm R_T = \pm$ 4.9 $\times$ 10$^{-4}$) allowed for $Z$ by $T$-invariance (obtained from the unitarity relation (8.26) and eq. (8.31)), and the narrow strip (width $\pm R_{CPT} = \pm$ 6.5 $\times$ 10$^{-4}$) allowed for $Z$ by $CPT$-invariance (obtained from the same unitarity relation (8.26) and eq. (8.34)). The cross denotes the present estimate for $Z$ and the curve enclosing $Z$ encloses all values for $Z$ lying within one standard deviation from the best estimate.

For $K_L^0 \to \pi\pi$ decay, the hyperweak hypothesis then leads to three definite predictions:

(*i*) $\eta_{+-} = \eta_{00}$, since both $K_S$ and $K_L$ decays are characteristic of the $K_+$ state. This implies $\varepsilon' = 0$.

(*ii*) $\eta_{+-}$ and $\eta_{00}$ have the phase $\varphi = 43^\circ$ given by eq. (8.17).

(*iii*) $\delta_L = 2Re\eta_{+-}$.

The present data are actually compatible with these predictions; the value of $\eta_{+-}$ leads to $2Re\eta_{+-} = (2.9 \pm 0.3) \times 10^{-3}$, which is quite consistent with the empirical value (8.7) for $\delta_L$. On the other hand, the experimental situation is far from satisfactory, in that the consistency between the various experiments for $\eta_{00}$ is exceedingly poor, so that the hyperweak hypothesis can only be described as an attractive possibility, not yet ruled out by experiment.

The particular attractiveness of the hyperweak hypothesis, apart from the fact that it leads to such definite predictions, is that these peculiar *CP*-violation effects are then relegated to a new category of weak interactions of much lower strength than the *CP*-conserving weak interactions with which we are now familiar. This picture is shown in Table II, which

TABLE II.

*The coupling strengths, strangeness selection rules, and status of the reflection symmetries C, P, T, are tabulated for the Strong interactions, the Weak interactions and the hypothetical Hyperweak interactions.*

| Interaction | Coupling Strength | $\Delta s$ | $C$ | $P$ | $T$ |
|---|---|---|---|---|---|
| Strong | $\sim 10$ | 0 | — | — | — |
| Weak | $\sim 10^{-5}$ | $\pm 1, 0$ | x | x | — |
| Hyperweak | $\sim 10^{-13}$ | $\pm 2 (\pm 1, 0?)$ | x | x | x |

shows how the hyperweak interactions would be placed relative to the strong and weak interactions. The hierarchy of interaction strength is also a hierarchy with respect to both the degree of strangeness-change involved and the degree of space-time reflection symmetry for the interactions. We do not understand why there should exist such a hierarchy of interactions but it is satisfactory at least that the interactions are placed in the same hierarchal order by these three different criteria.

*Other CP-violation Theories.* We shall not attempt to discuss in detail the many theoretical schemes which have been put forward concerning *CP*-violation [49]. Three straightforward possibilities may be mentioned:

(*i*) Milliweak Strong Interactions, which violate $C$ (and $T$, since $P$ holds good). These are possible because neither $C$ nor $T$ has yet been tested very precisely for the strong interactions. Combined with the weak interactions, they can lead to *CP*-violating decay processes.

(*ii*) Milliweak Weak Interactions, a new class of weak interactions with the usual strangeness selection rule ($\Delta s = 0, \pm 1$) but which violate not only $C$ and $P$ but also $T$.

(*iii*) $C$-violation for electromagnetic interactions, of order (1). These can then give rise to $CP$-violating weak interactions through virtual electromagnetic processes. It was suggestive [6] that $\alpha/\pi = 1/400$ is close to the relative magnitude of the $CP$-violating weak amplitudes. Despite considerable experimental effort, there are not yet any clear indications for such strong $C$ (and $T$)-violation effects (although the $np \to d\gamma$ detailed balance experiments do look suggestive). Much more experimental effort will have to go into checking $C$ and $T$ for electromagnetic processes; whether or not the $K_L \to \pi\pi$ decay processes arise from such interactions, it is clear that we must have stronger tests of these basic reflection symmetry properties for the otherwise so-familiar electromagnetic interactions.

The outstanding difficulty about an experimental program to test such $CP$-violation theories is that they do not make firm predictions which could provide crucial tests. However, much could be achieved if the experimental accuracies in this work could be pushed down to the level of $10^{-3}$ or lower, rather than the $10^{-2}$ accuracy at present achieved.

*Matter and Antimatter.* We are now left with the problem underlined by Landau. With the existence of $CP$-violating interactions, we are now able to distinguish left from right (and particle from antiparticle) in an absolute way by making appeal to the Laws of Physics, without making a direct contact comparison with the properties of the matter around us. We must emphasize here that to give the name *matter* to the material around us, i.e. to assign the baryon number $B = +1$ to our protons, is purely a convention. For example, we know that baryons of mass 938.62 MeV come in two varieties ($p$ and $\bar{p}$); the question is whether we can decide which variety the protonic particles in a far-off (or inaccessible) laboratory are, by experiments carried out there without any direct physical contact with our material.

It is worth-while to spend a little time to look at a definite set of instructions which we can use to instruct a man on a distant galaxy to carry out experiments which will enable us to decide whether or not his convention for «right-handedness» is the same as ours. This involves first being able to decide whether he is made of matter or antimatter, according to our convention. In doing so, we shall be following essentially the prescription suggested by Sakurai and Wattenberg [50], although

many other procedures could be followed. The instructions would run as follows:

« Define positive charge as the charge of your atomic nuclei, and the proton as the least massive of these nuclei. Construct a beam of pions which have negative charge, according to this convention, and use the reaction

$$\pi^- + p \to \Lambda + K^\circ \tag{8.36}$$

to form a $K^\circ$ beam in vacuum. Plot the distribution in proper time for each $K^\circ$ meson undergoing $\pi^+\pi^-$ decay, each time being taken from the point of production to the point of decay. You will find that this distribution has the form

$$P(t) = \left\{ exp\left(-\frac{t}{\tau_S}\right) + |\eta|^2\, exp\left(-\frac{t}{\tau_L}\right) + \right. \left. + 2\omega\,|\eta|\cos(\delta m_K t - \psi)\exp\left(-\frac{t}{2\tau_S} - \frac{t}{2\tau_L}\right)\right\}, \tag{8.37}$$

where $|\eta|$ is positive, the phase angle $\psi$ lies in the first quadrant, and $\omega = \pm 1$. Next, determine the helicity (by Bhabha scattering, for example) of the electronic particle resulting from the two-step decay sequence $\pi^+ \to \mu^+ \to e^+$ (averaged over all intermediate $\mu^+$ directions) for your positive pions, for the sense « right-handed » is given by the sense of, or by the sense opposite to, that helicity, according as you found $\omega = +1$ or $\omega = -1$ for the distribution (8.37) ».

If the far-off experimenter found $\omega = +1$, then his $K^\circ$ mesons are the same as our $K^\circ$ mesons and his galaxy is constructed from matter; therefore we agree in our definition of a $\pi^+$ meson and we both define right helicity from the resulting $e^+$ helicity. However, if the far-off experimenter found $\omega = -1$, then his $K^\circ$ mesons behave like our $\bar{K}^\circ$ mesons and we conclude that his galaxy is constructed from antimatter. When we tell him to take $\pi^+$ mesons, he will actually examine $\pi^-$ mesons (according to our convention) and the sense of the helicity he would determine from his resulting « $e^+$ helicity » will actually be our left helicity, since he will be determining the $e^-$ helicity for the sequence $\pi^- \to \mu^- \to e^-$ according to our conventions.

Thus we are once again faced with this perplexing result that it is possible to characterize a « right-handed » reference system in an absolute way by using the form of the Laws of Physics for these $CP$-violating interactions, to which we have again to accustom ourselves. It is probable that we are far from comprehending the full significance of the existence of forces in Nature which allow this possibility.

## 9. Conclusion.

At this stage, we are left with *CPT* as the only reflection symmetry which may still hold for all the forces in Nature. None of the data yet available is inconsistent with the validity of this *CPT* symmetry, and some of these data do test this principle in special ways to a high degree of accuracy. In fact, the violation of *CPT* invariance is difficult for us to envisage, as it would imply very basic changes from our present theoretical framework. In *S*-matrix theory, it would probably necessitate the introduction of non-analytic variables (distinguishing the forward from the backward light cone). As we have seen there would have to be a major upheaval in our field-theoretic approach to elementary particle physics, going beyond local commutativity at least, for there seems little else in either Lagrangian or axiomatic field theory which we could now imagine how to give up without upsetting such basic relationships as the connection between spin and statistics.

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# Geometrical Properties of the Fundamental Interactions.

## Introduction.

One can read in the scientific books written fifty years ago, that our whole universe is made up of three constituents: protons, electrons, and photons. This elegant view was destroyed in 1930 by one experiment performed in this town by Rasetti [1]: the measurement of the spin and statistics of the $N^{14}$ nucleus.

The following year four more particles were predicted: the neutrino by Pauli [2], the antiproton and the antielectron by Dirac [3] and the neutron which was expected by several groups. The last two were discovered after one year [4], [5], the first two, twenty five years later [6], [7]. The rate of discovery of particles has risen so sharply in the sixties that an exact count is at present uncertain. If you add to the photon, 8 leptons, 48 mesons, 111 baryons, and the corresponding antibaryons you reach a provisional total of 279. However, some physicists have not given up the hope of simplicity, and expect to build our universe with three quarks and their aintiquarks.

To others, the simplicity appears today in the small number of interactions among this crowd of different particles. As you all know there are in nature only four or five different interactions:

— gravitational, electromagnetic, nuclear or strong, weak and perhaps $CP$ violating.

Gravitational effects are so negligible at the microscopic scale that we shall not discuss them here. It is not yet clear whether the $CP$-violating interaction, discovered only five years ago and observed only in $K$-meson decay is a new interaction — which has then to be super weak — or a peculiar manifestation of the known ones.

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The strong, the electromagnetic and the weak interactions differ by their intensity, their range and their properties with respect to the transformations of the internal symmetry group. In this lecture we will however focus our attention not on these difference but on the striking similarity in the way the three interactions break the underlying symmetry (e.g. SU(3) × SU(3)). We will show that the directions defined in the internal symmetry space by *both* the electromagnetic and the lepton fields have simple and unique geometrical properties. The situation is more complicated for the strong interaction breaking. There exists several interesting approximations for its symmetry property: some of them have the same type of characteristic geometrical behaviour as the electromagnetic and the weak interactions.

## Strong Interaction Symmetry.

Strong interaction alone does not allow us to distinguish between baryons or mesons with different electric charge which belong to the same

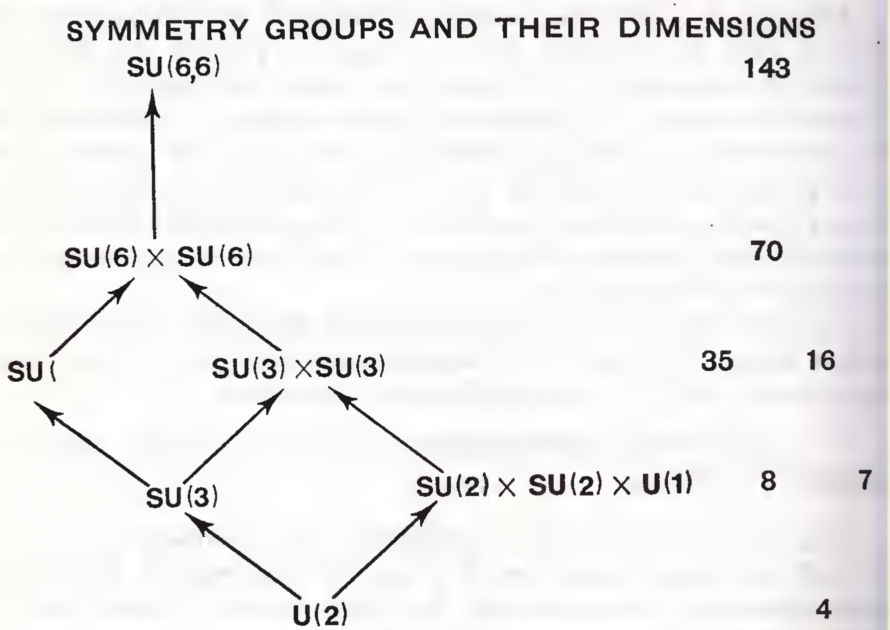


Fig. 1.

Lattice of internal symmetry groups used in hadronic physics; → means injection as subgroups.

isospin multiplet. This reflects the property of the strong interaction to be invariant under a group G larger than the Poincaré group $\mathcal{P}$. The

group G is the direct product $G = \mathcal{P} \times U(2)$. The U(2) symmetry is broken by the electromagnetic and weak interactions.

In recent years, larger and larger broken symmetry groups have been proposed for the physics of hadrons. They form the lattice of fig. 1.

The larger is the internal symmetry group, the coarser is the approximation in which this symmetry is exact.

Here we will consider the symmetry corresponding to $SU(3) \times SU(3)$ and its subgroups. $SU(3) \times SU(3)$ is the smallest group which couples in some way Poincaré invariance and internal symmetry. In the limit where the symmetry is exact, the full symmetry group is indeed the semi direct product (denoted by $\square$).

$$\mathcal{P}_0 \square [(SU(3) \times SU(3)) \square Z_2] = (\mathcal{P}_0 \times SU(3) \times SU(3)) \square Z_2$$

where $\mathcal{P}_0$ is the connected Poincaré group and $Z_2$ is the two element group generated by the space inversion $P$ which acts on $\mathcal{P}_0$ by an outer automorphism and *permutes* the two factors of $SU(3) \times SU(3)$.

## The Breaking of U(2) symmetry by the electromagnetic and weak interactions.

We can understand this breaking by analogy with the Zeeman effect. When an atom (which is a physical system with a rotational symmetry) is placed in a magnetic field $\vec{B}$, one must add to the Hamiltonian the interaction term

$$H = \int \vec{B} \cdot \vec{\mu}\,(x)\, d^3x \tag{1}$$

where $\vec{\mu}(x)$ is the vector operator representing the magnetic moment density. Of course $\vec{B} \cdot \vec{\mu}$ is invariant under rotations, but the rotational symmetry is broken because the magnetic field marks a preferred direction. Similarly, we can say that the electromagnetic interaction marks a preferred direction $q$ in the vector space of the Lie algebra of U(2). The U(2) Lie algebra is a direct sum $U(1) \oplus SU(2)$: the U(1) corresponds to the hypercharge $y$, the SU(2) is spanned by three orthonormal isospin vectors $t_i$ $(i = 1, 2, 3)$ which are chosen by a traditional convention. The direction $q$ singled out by the electromagnetic interaction is

$$q = t_3 - \frac{1}{2} y\,. \tag{2}$$

This is the Gell-Mann-Nishijima relation [8].

It would make no sense to say that we can recognize a direction if we were not able to recognize all the others and therefore orient our-

selves in the U(2) space. Two other directions $t_1$ and $t_2$ can be recognized with the help of the weak hadronic currents for $\beta$-decay. The strong mass splitting and the hypercharge conservation by strong and electromagnetic interactions allow us to recognize the direction $y$.

The analogy with the interaction in a constant external magnetic field goes even deeper. Indeed according to the assumption of Feynmann and Gell-Mann [9] the vector part of the weak hadronic currents $v_\mu^\pm(x)$ and the electromagnetic current $j_\mu(x)$ are three components of the same, U(2) vector operator $\vec{v}(x)$. In analogy to (1), the electromagnetic and weak interaction terms of the Hamiltonian can be written as:

$$H_{em} = e\int \vec{A}^\mu(x)\cdot\vec{v}_\mu(x)d^3x \tag{3}$$

$$H_w = \frac{G}{\sqrt{2}}\int \sum_{\varepsilon=\pm 1} \vec{L}^\mu_{(\varepsilon)}(x)\cdot \vec{v}^{(\varepsilon)}_\mu(x)d^3x \tag{3'}$$

where $L^\mu_{(\pm)}(x)$ are the charged $\pm$ leptonic currents which single out the directions $t_1 \pm it_2$ of the complexified vector space of U(2) in the same way as the electromagnetic field $A^\mu(x)$ distinguishes the direction $q$.

Thus even though we cannot change the directions of the external fields (as we could do for the magnetic field of our example) we can nevertheless orient ourselves completely in the U(2) space since the vectors $y$, $q_1$, $t_1$ and $t_2$ span the whole space of the U(2) Lie algebra.

## Currents as tensor-operators.

Let us recall the definition of tensor-operators, these fundamental tools for the expression of group invariance in quantum mechanics. Given a Lie group G represented by unitary operators $\in \mathcal{L}(\mathcal{H})$ acting on the Hilbert space $\mathcal{H}$ of states, an $\mathcal{E}$-tensor operator is an intertwinning operator between the vector space $\mathcal{E}$ of a linear representation of G and the space $\mathcal{L}(\mathcal{H})$. If $\mathcal{G}$ is the real vector space of the Lie algebra of G, there is a remarkable tensor operator $F$ whose image is the set of self adjoint « group generators ». They form a representation up to a factor $i$ of the Lie algebra.

$$\forall a, b \in \mathcal{G}\,, \qquad [F(a), F(b)] = iF(a \wedge b) \tag{4}$$

where $\wedge$ denotes the Lie algebra law. Let the representation of $\mathcal{G}$ on $\mathcal{E}$ be: $a \to D(a)$; an $\mathcal{E}$-tensor operator $\mathcal{E} \xrightarrow{T} \mathcal{L}(\mathcal{H})$ can be equivalently defined by the relation

$$\forall a \in \mathcal{G}, \forall r \in \mathcal{E}\,, \qquad [F(a), T(r)] = iT(D(a)r)\,. \tag{5}$$

As we have seen, electromagnetic and hadronic weak vector currents are the images in the directions $q$ and $t_1 \pm it_2$ of the same $\mathcal{G}$-tensor operator where $\mathcal{G}$ is the Lie algebra of U(2). We will thus write: $v_\mu(x, q)$ and $\frac{1}{2} v_\mu(x, t_1 \pm it_2)$ for the electromagnetic and weak vector currents respectively. After the extension of the strong interaction invariance group [10] from U(2) to SU(3) Cabibbo's hypothesis [11] extended the variance of these currents. They became octet-operators where the octet-space is the eight dimensional space $\mathcal{E}_8$ of the Lie algebra of SU(3). With the Cartan Killing form this is an euclidean space and from now on, we shall use only unit length vectors (belonging to the unit sphere $S_7 \subset \mathcal{E}_8$).

Explicitely,

(6) $\qquad$ electromagnetic currents $\displaystyle = \frac{2}{\sqrt{3}} v^\mu(x, q)$

(6′) $\qquad$ weak vector currents $\displaystyle = \frac{1}{2} v^\mu(x, c_1 \pm ic_2)$

(6″) $\qquad$ weak axial vector currents $\displaystyle = \frac{1}{2} a^\mu(x, c_1 \pm ic_2)$ .

Indeed Cabibbo also assumed that the axial vector and weak vector currents are two different octet operators, but in the *same* directions $c_1$ and $c_2$. These directions are different from $t_1$ and $t_2$ in order to take into account the hypercharge violating weak transitions; they make an angle $\theta$ (= Cabibbo's angle) with the former directions. The total hadronic weak current that we denote by

$$h^\mu(x, c_i) = v^\mu(x, c_i) - a^\mu(x, c_i) \tag{7}$$

is therefore another octet-operator.

In the next section we will show the geometrical properties of the physical directions appearing in (6), (6′) and (6″).

## Some geometrical concepts. Their application to the SU(3) octet.

The SU(3) linear action in the octet space $\mathcal{E}_8$ distinguishes some directions [12]. When a group G acts on a set $M$, the set of all transforms of a given point $p \in M$ is called the orbit G($p$) of $p$ and the set of all group elements leaving $p$ fixed is a subgroup $G_p \subset G$ called the little group or

the isotropy group of $p$. Two points of a same orbit have conjugated little groups. We call stratum the set of all points with the same little group up to a conjugation and the orbits of a stratum are said of the same type. To summarize, by the action of G, the set $M$ is partitionned into strata which are partitionned into orbits of the same type. When G is a compact Lie group acting differentiably on the compact manifold $M$, there is a stratum (called generic) which is open dense. For example in the action of SU(3) on the unit sphere $S_7 \subset \mathcal{E}_8$, the generic stratum is a one parameter set of 6 dimensional orbits, whose little groups are the Cartan subgroups ($\sim U_1 \times U_2$) of SU(3). There is one more stratum composed of two four-dimensional orbits. Their elements will be called exceptional vectors; they have a larger little group: U(2). The hypercharge and electric charge directions $y$ and $q$ are such exceptional vectors. Their little groups are denoted by $U_y(2)$ and $U_q(2)$ and their semi-simple part $SU_y(2)$, $SU_q(2)$ are called the isospin and $u$-spin groups in the physics literature. The orbits of exceptional vectors have the following properties:

1) *they are critical*; this means: consider a differentiable real function $f$ on $M$, invariant by G (i. e. constant on the orbits). Its differential $df_p$ at $p$ is an element of the dual of the vector space $T_p(M)$, the plane tangent to $M$ at $p$. An orbit of G on $M$ is critical if for *all* G-invariant real differentiable functions $f$ on $M$, $df = 0$ on the orbit. In table 1 we list all examples of critical orbits which we discuss here.

2) *their vectors are idempotents of the canonical symmetrical algebra*; consider a compact Lie group G and an irreducible linear representation $D$ on $\mathcal{E}$. If in the reduction of the tensor representation $D \otimes D$ on $\mathcal{E} \otimes \mathcal{E}$, the irreducible representation $D$ appears once and only once in the symmetrical part of the tensor product, the corresponding intertwinning operator $V$ (defined up to a multiplicative factor) $\mathcal{E} \otimes \mathcal{E} \xrightarrow{V} \mathcal{E}$ defines a symmetrical algebra

$$V(x \otimes y) = x \vee y = y \vee x \tag{8}$$

which has G as group of automorphisms. Such a canonical symmetrical algebra exists for the adjoint representation of the classical simple Lie groups only for the SU($n$), $n \geq 3$. That of SU(3) has been studied by Gell-Mann who denoted by $d_{ijk}$ its structure constants.

An idempotent vector of this algebra satisfies

$$x \vee x = \lambda x \,. \tag{9}$$

This equation is obtained in all SU(3)-invariant bootstrap models that we have seen published [13].

Properties 1) and 2) are not unrelated. For every real irreducible linear representation of a compact Lie group G, there exists an invariant euclidean scalar product. For a representation of G, on $\mathcal{E}$, which possesses a canonical symmetrical algebra, one can define:

$$\{x, y, z\} = (x \vee y, z) . \tag{10}$$

This is a trilinear invariant, completely symmetrical under the permutation of $x$, $y$, $z$ and any differentiable function $f(\mu)$ with $\mu = \{x, x, x\}$ defined on the unit sphere $(x, x) - 1 = 0$, is G-invariant. In order to find its extrema, one has to vary the function $f(\{x, x, x\}) - \lambda'(1 - (x, x))$ where $\lambda'$ is a Lagrange multiplier. This yields equation (9) with $\lambda = \frac{2}{3} \lambda'(df/d\mu)^{-1}$.

Since we are interested only in the directions of the vectors of $\mathcal{E}_8$ we should probably consider, instead of the unit sphere $S_7$, the real projective space $P_7$ which is the set of directions of $\mathcal{E}_8$. ($P_7$ is obtained from $S_7$ by identifying the two points of each diameter). In the action of SU(3) on $P_7$ there are 3 strata: the generic one (little group $U(1) \times U(1)$); another one consisting of the critical orbit of exceptional vectors (defined up to a sign, (little group $U(2)$) and finally the stratum which contains the orbit of the root-vectors of the SU(3)-Lie algebra (little group $(U_1 \times \times U_2)\,\square\, Z_2$). This orbit is also critical, but equation (9) defined on $\mathcal{E}_8$, does not apply to its vectors. It is remarkable that the physical directions $c_1$ and $c_2$ belong to this new critical orbit.

Given a unit root-vector $s$, then $\sqrt{3}\; s \vee s$ is a unit exceptional vector. The exceptional vector $z$ defined by the weak interaction:

$$(c_i, c_j) z = \sqrt{3}\; c_i \vee c_j \tag{11}$$

with

$$i, j = 1, 2, 3 \; ; \qquad c_3 = c_1 \wedge c_2 \tag{12}$$

is sometimes called the direction of the weak hypercharge. It is possible that this direction can be observed physically. Indeed the most commonly proposed form of non leptonic weak interaction is

$$H_{N.L.} = \frac{G}{\sqrt{2}} \sum_{\varepsilon = \pm 1} \int h^{\mu}\left(x, \frac{c_1 + i\varepsilon c_2}{2}\right) h_{\mu}\left(x, \frac{c_1 - i\varepsilon c_2}{2}\right) d^3x \tag{13}$$

with the drawback that $H_{N.L.}$ is the image of a reducible tensor operator with some component in the « 27 » irreducible representation of SU(3).

The $\Delta T = \frac{1}{2}$ rule for the weak transitions with $|\Delta y| = 1$ suggests that this 27 component is negligible compared to the octet component. According to the proposal of one of us [14], the non-leptonic Hamiltonian would instead be

$$H_{N.L.} = \frac{G}{\sqrt{2}} \int (h^{\mu}(x) \vee h_{\mu}(x))\,(z)\, d^3x\,, \tag{14}$$

i.e. it would be the component along the weak hypercharge $z$ of an irreducible octet-tensor operator. This proposal seems to be compatible with the known experimental data.

Let us finally note that $y$ and $z$ define $q$:

$$q(1 - (y, z)) = \sqrt{3}\, y \vee z + \frac{1}{2}(y + z) \tag{15}$$

where

$$(y, z) = 1 - \frac{3}{2} \sin^2 \theta\,. \tag{15'}$$

## The $(SU(3) \times SU(3))_{\square} Z_3$ symmetry [15].

The $SU(3) \times SU(3)$ symmetry becomes an exact symmetry of the hadronic world when the masses of the octet of pseudoscalar mesons are neglected. Remark that it is not a much more crude approximation to neglect these masses than to neglect their differences as it is already implied by SU(3). As a matter of fact a much milder approximation than SU(3) is to neglect only the $\pi$-meson mass (only 140 MeV which is smaller than the mass differences within the octet of pseudoscalar mesons). This corresponds to considering a $SU(2) \times SU(2) \times U(1)$ subgroup of $SU(3) \times SU(3)$. The SU(3) discussed in the previous section is the diagonal subgroup of $SU(3) \times SU(3)$. The two SU(3) factors are called the chiral $SU^{\pm}(3)$. The vector space $\mathcal{E}_{16}$ of the Lie algebra of $SU(3) \times SU(3)$ is a direct sum of two octet spaces

$$\mathcal{E}_{16} = \mathcal{E}_8^{(+)} \oplus \mathcal{E}_8^{(-)} \tag{16}$$

whose vectors we denote by

$$a = a^+ \oplus a^-\,. \tag{17}$$

On this space there is a $SU(3) \times SU(3)$ invariant euclidean scalar product

$$(\tilde{a}, \tilde{b}) = \frac{1}{2}(a^+, b^+) + \frac{1}{2}(a^-, b^-)\,. \tag{18}$$

The Lie algebra is

$$\tilde{a} \wedge \tilde{b} = (a^+ \wedge b^+) \oplus (a^- \wedge b^-) \tag{19}$$

and the canonical symmetrical algebra is

$$a \vee b = (a^+ \vee b^+) \oplus (a^- \vee b^-) \,. \tag{20}$$

The electromagnetic current, the vector part and the axial part of the weak hadronic currents are all in the image of the same $\mathcal{E}_{16}$-tensor operator $h(x, \tilde{a})$ for the directions:

$\tilde{q} = q \oplus q$ for the electromagnetic current

$\tilde{c}_1 \pm i\tilde{c}_2$, with $\tilde{c}_i = 0 \oplus c_i$ for the weak current

and

$\tilde{z} = 0 \oplus z$ is the direction of the weak hypercharge.

The symmetrical algebra has only two different types of idempotents and $\tilde{q}$ *and* $\tilde{z}$ *are two examples of these two types.*

The orbit of $\tilde{z}$ on $S_{15}$ is critical for the $SU(3) \times SU(3)$ action, whereas the orbit of $\tilde{q}$ is not. It becomes critical when the group is extended to $(SU(3) \times SU(3))_{\square}Z_2$ i. e., as we have seen, when one takes into account space reflexions.

When we go over to the projective space $P_{15}$, two new types of critical orbits appear.

— One corresponds to the root vectors of $SU(3) \times SU(3)$ and the physical directions $\tilde{c}_1$ and $\tilde{c}_2$ are illustrations of this case;

— The other type can be represented by the orbit of unit vectors (up to sign) such as

$$s \oplus \pm s$$

where $s$ is a root vector of $SU(3)$. This orbit contains vectors of opposite parity [1].

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[1] For instance the image of this orbit by the current, $h_\mu(x, \tilde{a})$ contains both vectors $\tilde{a} = \pm (s \oplus s)$ and pseudovectors $\tilde{a} = \pm (s \oplus - s)$ which are transformed into each other by $SU(3) \times SU(3)$.

## The Breaking of the $(SU(3) \times SU(3))_\square Z_2$ by the Strong Interaction.

In the paper in which he introduced this larger symmetry, Gell-Mann [10] proposed that the breaking of $SU(3) \times SU(3)$ due to the strong interactions occurs through a tensor operator of the

$$(3, \bar{3}) \oplus (\bar{3}, 3)$$

representation.

This 18-dimensioned representation, which is irreducible for $(SU(3) \times \times SU(3))_\square Z_2$, appears naturally in the quark model and SU(3) (the diagonal subgroup of $SU(3) \times SU(3)$) is then the little group of the direction of $\mathcal{E}_{18}$ along which the symmetry is broken in the SU(3)-approximation. In a more recent paper Gell-Mann, Oakes and Renner [16] have suggested that the direction of the breaking in $\mathcal{E}_{18}$ is in fact closer to the direction invariant under $SU_y^+(2) \times SU_y^-(2) \times U_y^d(1)$ (where $d$ means diagonal).

TABLE I.

| Group | Manifold | Number of critical Orbits in the Stratum | Dimension of critical Orbits | Little Group | Example of Vectors belonging to the critical Orbit |
|---|---|---|---|---|---|
| a) SU(3) | $S_7$ | 2 | 4 | U(2) | $\pm y, \pm q, \pm z$ |
| b) SU(3) | $P_7$ | 1<br>1 | 4<br>6 | U(2)<br>$C = (U_1 \times U_1)_\square Z_2$ | $y, q, z$<br>$c_1, c_2$ |
| c) $(SU(3) \times SU(3))_\square Z_2$ | $S_{15}$ | 2<br>2 | 4<br>8 | $SU(3) \times U(2)$<br>$(U(2) \times U(2))_\square Z_2$ | $\pm \tilde{z} = 0 \oplus z$<br>$\pm \tilde{q} = q \oplus q$ |
| d) $(SU(3) \times SU(3))_\square Z_2$ | $P_{15}$ | 1<br>2<br>1<br>1 | 4<br>8<br>6<br>12 | $SU(3) \times U(2)$<br>$(U(2) \times U(2))_\square Z_2$<br>$SU(3) \times C$<br>$(C \times C)_\square Z_2$ | $\tilde{z}$<br>$\tilde{q}$<br>$\tilde{c}_i = 0 \oplus c_i$<br>$\tilde{s} = s \oplus \pm s$ |
| e) $(ZU(3) \times SU(3))_\square Z_2$ | $S_{17}$ | 1<br>2 | 9<br>8 | $SU_y^+(2) \times SU_y^-(2) \times U_y^d(1)$<br>$SU^d(3)$ | |

This table lists the critical orbits for the group action on real manifolds used in text.

The critical orbits are manifolds of smaller dimension. The last column gives examples of points of the critical orbits; they all correspond to the directions of the interactions with the possible exception of the last one.

On the space $\mathcal{E}_{18}$ of the $(3, \bar{3}) \oplus (\bar{3}, 3)$ representation there exists a symmetrical canonical algebra with two kinds of idempotents,

$$x + x = \lambda x \,. \tag{21}$$

One kind of unit vector solution $\left(\lambda = \sqrt{\frac{2}{3}}\right)$ corresponds to two critical orbits (see Table I) of $(\mathrm{SU}(3) \times \mathrm{SU}(3))_{\square}\mathrm{Z}_2$ on $\mathrm{S}_{17}$ with little group $\mathrm{SU}^d(3) \times \mathrm{Z}_2$.

The other kind ($\lambda = 0$, nilpotent elements) corresponds to a critical orbit with little group

$$(\mathrm{SU}_y^+(2) \times \mathrm{SU}_y^-(2) \times \mathrm{U}_y^d(1))_{\square}\mathrm{Z}_2 \,.$$

These two solutions of (21) are parity conserving and correspond to the two physically interesting breakings of $\mathrm{SU}(3) \times \mathrm{SU}(3)$ with approximate $\mathrm{SU}(3)$ or $\mathrm{SU}(2) \times \mathrm{SU}(2) \times \mathrm{U}(1)$ invariance for the strong interactions.

## Open Problems.

The Cabibbo angle $\theta$ establishes the relative orientation of the frames in the spaces of the two representations: the adjoint representation $(1, 8) \oplus (8, 1)$ and the $(3, \bar{3}) \oplus (\bar{3}, 3)$. Probably $\theta$ is a projective invariant built with the vectors which are singled out in these two spaces by the different interactions. We do not expect however that the value of $\theta$ could be obtained from purely geometrical considerations.

The nature of the *CP*-violating interaction is another open question. It might be a new interaction or, as in many models that have been proposed, it may correspond to a small *T*-violating term of the weak or electromagnetic interactions. It may even be that *CP*-violation is, as Good, Michel and de Rafael [17] have proposed, a collective effect of the three interactions (weak, electromagnetic and strong) which disappears when some parts of any one of them is turned off.

In any case one expects that the *CP*-violating transitions will also single out some direction of a $\mathrm{SU}(3) \times \mathrm{SU}(3)$ representation space. As we have seen, all the critical orbits of $(\mathrm{SU}(3) \times \mathrm{SU}(3))_{\square}\mathrm{Z}_2$ on $P_{15}$ except for one, correspond to the breakings of $\mathrm{SU}(3) \times \mathrm{SU}(3)$ by the electromagnetic and the weak interactions. It might be that the *CP*-violating transitions choose the unused type of critical orbit listed in Table I.

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## Conclusion.

The breakings of $(SU(3) \times SU(3))_{\square}Z_2$ induced by the coupling of hadrons to the electromagnetic field and to the lepton currents occur respectively in the directions $\tilde{q}$ and $\tilde{c}_1$, $\tilde{c}_2$ of the space $\mathcal{E}_{16}$ of the adjoint representation $((8.1) \oplus (1.8)$. We have shown that in the action of $(SU(3) \times \times SU(3))_{\square}Z_2$ on the corresponding projective space $P_{15}$ the orbits to which the above directions belong are critical. In the same space $P_{15}$ there are two other critical orbits. One of them contains the weak hypercharge direction $\tilde{z}$ and one of us has suggested [14] that it could be associated with the non-leptonic weak interactions. We wonder if the preferred direction which appears in the $CP$-violating interaction might not belong to the remaining critical orbit as suggested by the model of ref. [17].

On the unit sphere $S_{17} \subset \mathcal{E}_{18}$ (the space of the $(3.\bar{3}) \oplus (\bar{3}.3)$ representation) the action of $(SU(3) \times SU(3))_{\square}Z_2$ creates two types of critical orbits. Their little groups (up to a conjugation) are $SU^d(3)$ and $SU^+_y(2) \times \times SU^-_y(2) \times U^d_y(1)$. They correspond to the two interesting approximations for the breaking of $SU(3) \times SU(3)$ by the strong interaction. The actual direction of the strong breaking is in between those two and its determination is probably related to that of the Cabibbo angle.

In our opinion the notion of critical orbit is very important for understanding the breaking of symmetries. For hadronic physics this notion appears only when one enlarges the isospin group. Indeed in the three dimensional space all directions are transformed into each other by the action of the rotation group.

As we have seen critical orbits appear naturally in a bootstrap model or in a model blending a variational principle with group invariance. The success or the failure of such models will then be independent of dynamical details but rest only on the physical choice of the invariance group and of the space on which it acts.

In conclusion, we believe that the qualitative mathematical concepts which appear in the study of group action on manifolds have helped us to formulate the empirical laws of the breaking of the internal symmetry in an aesthetical and concise form. This formulation might prove to be well adapted to a future more fundamental explanation.

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S. FUBINI (*)

# Dynamics of Strong Interaction.

If we wish to summarise briefly the present situation in strong interaction physics we can say that we are still rather far from any fundamental understanding of the matter. We have also not been able to obtain a phenomenological scheme for elementary particles which is as successful as the Mendeleev table for chemical elements.

One can attribute this unsettled state of things to the fact that experimental information in our field is so hard to get. The discovery and the analysis of a new isobar is a very hard operation both in terms of money and of time. One can hope that when and if the famous quarks will be discovered our difficulties will miracolously disappear and that a description of elementary particles as satisfactory as the one of atoms and of molecules will soon be obtained.

It is however my opinion that the main reason for our troubles is indeed theoretical. In our field we are facing for the first time a case in which quantization is important and energies are extremely relativistic.

Now although it has been possible in several cases to obtain peaceful coexistence between the requirements of quantum mechanics and those of special relativity, we do not yet have a theoretical scheme in which both theories combine in a general consistent way.

In elementary particle physics this leads to a very peculiar new situation.

In any scattering problem the physical amplitude must satisfy several constraints, independent on the detailed dynamics of the problem, for example conservation laws, unitarity and reasonable analytic properties.

In our extremely relativistic case those contraints become so stringent and numerous that nobody has yet found a non trivial example of

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an amplitude which does not violate at least one fundamental requirement. One of the reasons for this situation is that in our problem one single amplitude represents at the same time several processes, since we can interpret the external lines both as incoming particles or outgoing antiparticles (substitution rule).

For example the amplitude for the process

$$A + B \longrightarrow C + D \tag{1}$$

should also represent the " crossed processes "

$$A + \overline{C} \longrightarrow \overline{B} + D \tag{2}$$

$$A + \overline{D} \longrightarrow \overline{B} + C\,. \tag{3}$$

So it usually happens that if we have succeded in obtaining a perfectly satisfactory amplitude for the reaction (1), this amplitudes gives an unpleasant behaviour for (2) or (3) or both.

A possible approach is to construct the theory starting from a relativistic invariant Lagrangian. In this way we should be assured that we don't violate any fundamental requirement. However it so happens that only a very few Lagrangians exist whose theoretical treatment is at present possible and even in those favourable cases people have succeded in obtaining finite consistent results only when the coupling constant is small.

The fact that the field theoretical approach has not been too fruitful has led several theorists to work directly with the physical scattering matrix and to translate the different constraints into integral or albegraic equations for the matrix elements.

A possible criticism to this bootstrap idea is that there is no dinamics in it. However, the existence of the substitution rule makes the usual separation between kinematics and dynamics somewhat meaningless.

For example the process

$$N + N \rightarrow \pi \rightarrow N + N \tag{4}$$

seen in the crossed channel reads

$$\begin{aligned} &N_1 \rightarrow N_1 + \pi \\ &N_2 + \pi \rightarrow N_2\,. \end{aligned} \tag{5}$$

The reactions (5) represent the pion exchange between the two nucleons which is responsible for an important contribution to nuclear forces.

There are sometimes strong difference of opinion between people advocating bootstrap or field theory.

However there is a lot in common between the two approaches: both of them meet great difficulties and the origin of those difficulties is probably the same.

If one looks at the development of the bootstrap program one sees different lines of investigation, which differ in the kind of approximation which is being used.

First of all a low energy bootstrap approach was attempted.

It was based on the idea that low energy reactions in which only the two body channel is open, can in some way be decoupled from the effects at higher energies.

This allowed to take into account reasonably well unitarity which, in the two body problem, takes a particularly simple form.

The method was quite successful in giving the first systematization of low energy pion physics, but led to great difficulties for " more relativistic " problems like pion-pion scattering.

The " multiperipheral approach " concentrates on high energy phenomena and leads to a reasonable description of the main effects in this energy range. It leads to a beatiful explanation of the Regge behaviour and to general predictions about spectra, multiplicity which are in reasonable agreement with experiment.

The so-called " multiperipheral bootstrap" tries to obtain in a self consistent way the parameters of the dominating Regge trajectories. Work in this very interesting direction is in progress.

A new interesting development has come about during the last years. The idea is to try an approximation to the S matrix in terms of the exchange of narrow resonances. This is in agreement with the experimental finding of more and more metastable states of small width.

Also here the substitution rule plays a very important role.

It is easy to be convinced that the simple formula expressing the exchange of one resonance in one channel does exhibit a bad asymptotic behaviour in the crossed channel.

So if we want to construct a model based on resonant states, we have to introduce many levels and adjust them in such a way that there is a cancellation between the different terms. This of course leads to algebraic relation between the different masses and coupling constants.

This approach was first carried out by writing down a set of dispersion sum rules and saturating them by means of one particle states. The

results where indeed rather encouraging, but it was hard to carry out the program in a general systematic ways.

Now, following an important suggestion by Gabriele Veneziano, it is possible to write down general resonant amplitudes for many body problems where the compensation is such that the asymptotic behaviour is good in all channels.

Of course many problems have still to be understood before we can say that these new ideas have developed in a full fledged theory. Several years of hard work are before us, however I am convinced we are now on the right track to a satisfactory understanding of the strong interaction between elementary particles.

T. REGGE (*)

# S-matrix Theory of Elementary Particles.

After Murray Gell-Mann's talk it has become almost imperative to produce some statement clarifying my role either as Newtonian type or as Mendeleevian type of physicist. During this talk I shall adopt an unmistakably Newtonian point of view in spite of the repeated warnings by Gell-Mann that this may not be the right time to attempt a dynamical synthesis as comprehensive as the one achieved by classical mechanics at its appearance. At the same time I would like to point out at once that today's talk will not contain any theory, whether in a complete or preliminary form. It deals rather with a set of recommendations and with a list of technical problems to be solved as a preliminary step toward the construction of a theory of the $S$-matrix. In this sense we are merely contented to point out what are the natural questions to ask about the (so far undefined) $S$-matrix.

As we all know, the first actual use of the $S$-matrix in a rather simplified context goes back to J. A. Wheeler, but Heisenberg is the one who realized its importance and its most important properties in connection with the theory of elementary particles. In more recent time, G. Chew has systematically emphasized the autonomous role of the $S$-matrix type of theory versus the conventional field theory, and he has proposed a set of axioms (or principles) for the construction of the $S$-matrix. There is no doubt that, although I do not share completely the outlook of Chew on the $S$-matrix, at the same time I am deeply conditioned by his thinking.

According to Chew's first degree analyticity, a given $S$-matrix element as function of the momenta of the participating particles should have singularities at the physical multiple processes. In his words, a multiple process is one that proceeds via a succession of two or more macroscopically separated collisions. As Coleman and Norton have pointed out the rules for such a multiple process are the same as the Landau rules for Feynman relativistic amplitudes (*FRA*). As there is a discrete infinity

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of possible $FRA$ interpolating given sets of initial and final multiparticle states, each $S$-matrix element has a singular locus consisting at least of the union of infinitely many Landau varieties for each graph. Besides these singularities, we have also the second kind or non-Landau singularities whose discussion is a good deal more complex than for the ordinary singularities. It is quite reasonable to assume with Chew that single particle singularities are polar ones and that higher singularities are branching loci of either the logarithmic or square root type according to simple rules deduced by Landau in his famous paper.

In this way, starting from the physical sheet as defined in some sufficiently small regular neighbourhood $U$ of a suitable base point $B$, we may arrive at other Riemann sheets of the same multivalued analytic function. In general, we expect that these new Riemann sheets will be infinite in number and that they will be related to the physical sheet through discontinuities. These in turn can be expressed as unitary integrals over amplitudes of different processes. We expect therefore that the unphysical Riemann sheets, in spite of their name, will be just relevant to physics as the physical sheet. We owe Poincaré a splendid formalism for the systematical description of the collection of Riemann sheets of an analytic multivalued function in terms of the so-called fundamental group (also named $\pi_1$ or first homotopy group). We shall explain the idea of Poincaré in a rather idealized situation. We suppose that a pair of complex algebraic varieties be given $X \supset L$ and that we intend to describe a multivalued function $f(z)$ $z \in X - L$ analytic on $X - L$, having $L$ as a branching locus. We select a point $B \in X - L$ and a nonsingular neighbourhood $U$ of $B$. In this case a given arc in $X - L$ with initial and final point $B$ will give rise in general to a nontrivial analytic continuation of the initial determination (physical sheet) of the scattering amplitude defined in $U$. Two arcs, however, which can be deformed into each other within $X - L$ while their end points are kept fixed will produce the same final determination of the function $f(z)$. The important object is then the class of loops which can be deformed into each other under these conditions. It is easily seen that this kind of mutual deformability is an equivalence relation and that we are dealing with equivalence classes. In this sense when we speak of loops we really mean the corresponding equivalence class. The important step taken by Poincaré was to recognize that the set of classes can be given a natural group structure (written $\pi_1(X - L, B)$ or shortly $\pi_1$). In this group the identity is the trivial loop which encloses no singularity and can be shrunk within $U$. The product $\alpha\beta$ of the loops $\alpha$ and $\beta$ is the loop obtained by continuing first along $\beta$ and then $\alpha$. The inverse of $\alpha$ is the same loop with the opposite orientation. $\pi_1(X - L)$ displays then all Riemann sheets with the additional infor-

mation of the group structure. I feel that this group structure has been largely underestimated and ignored even by physicists who are quite enthusiastic users of the customary Riemann multisheeted picture and of group theory. There is no doubt that the group picture is at least more economical. Furthermore, we cannot consider the fundamental groups are the latest exotheric mathematical whim for it was conceived before relativity.

The first question is then whether $\pi_1$ can be defined at all for a given element of the $S$-matrix. The difficult point here is that $L$ is actually the union of an infinite set of Landau varieties. This set will be everywhere dense and a direct definition of $\pi_1$ as the one sketched before is no longer possible because then every point in $X$, being a limiting point of a singular set, would be itself singular and our scheme would fall apart. A milder form of this disease could be the Karplus-Freund natural boundary. While our question remains relevant, there could be some interesting ways of averting disaster. We may first observe that practically we may measure and observe a given matrix element only over a finite range of values of the relevant variables in momentum space and that physics necessarily deals with compact sets only in momentum space. Now it may as well be that although the set of Landau varieties is infinite $L = \bigcup_1^\infty L_p$ only a finite number of them $\bigcup_p^n L_p$ can be actually singular for the class of Riemann sheets obtained by continuing inside a given compact set $O$. In this case $\pi_1(O - \bigcup_1^n L)$ is perfectly well defined for we need not subtract from $O$ a perfectly well behaved set. If this turns out to be the case, we may abandon the idea of constructing directly $\pi_1(X - L)$ and use instead some suitably defined limit on a monotonic sequence of compact sets, for instance a sequence of balls of radius R, where R tends to infinity. I find this procedure more appealing than the straight attempt to define $\pi_1(X - L)$ and probably easier to carry out. But of course nothing can be done unless somebody proves our conjecture. To this purpose I notice that it is a well known fact that positive Landau surfaces tend to move away as the complexity of the graph increases. To my knowledge a clear and general statement on this property has not yet been published. Once the fundamental group $\pi_1(X - L)$ or $\pi_1(O - \bigcup_1^n L_r)$ has been constructed, we may ask how does its knowledge relate to the (possibly numerical) knowledge of the $S$-matrix. I shall attempt to answer the question in two steps. The first step is to ask the same question for a given Feynman graph. There is no doubt that Feyn-

man graphs give a very crude information on the $S$-matrix (with the exception of the celebrated numerical agreements in electrodynamics). On the other hand, they share their own set of singularities with the $S$-matrix and therefore their fundamental group is certainly a factor group of that of the $S$-matrix. They are therefore the natural testing ground for many of the conjectures and methods to be used later (if ever) on the $S$-matrix. In this sense I have begun (in collaboration with Ponzano, Westwater and Speer) a systematic investigation of increasing classes of graphs although we have no intention of taking perturbation theory seriously. We have now under complete control the self energy graphs with two vertices and an arbitrary number of connecting lines and the single loop graphs.

In carrying out this investigation we have considered as variables also the internal and external masses. Therefore technically we are as far removed from the original Heisenberg-Chew philosophy as possible. The reasons for doing this are many. First of all the structure becomes far more symmetrical and the formalism simpler. Secondly, if an internal line of a graph is replaced by two lines, in order to know the analytic properties of the new graph, even for fixed internal masses, we need to know the corresponding properties of the old graph in the replaced mass. Thirdly, it is generally trivial to specialize the relevant variables on the shell once the problem is solved in the utmost generality. In what follows therefore, I shall assume that also the masses in the theory are complex variables. I have no doubt that here I shall collide against many colleagues for whom, for instance, the proton electron mass ratio $m_p/m_c$ is implicitly fixed by the structure of the $S$-matrix. In view of the present nebulous state of affairs of the theory, I can only state my ignorance and lack of commitment on the specific mechanism by which this and other dimensionless constants of nature are fixed. It might as well be that a whole set of perfectly reasonable $S$-matrices exist for any choice of these parameters, all of them yielding rather weird self-consistent universes, all but one of the existing only in the sense of Plato. Our universe would be determined by the fact that only the choice $m_p/m_c = 1837$ ... etc. guarantees that there are long chain molecules of the right kind and size as to make biological phenomena possible. It could be for instance that the slightest variation in these parameters would change critically the size and length of the rungs in the DNA helix as to invalidate its typical way of replicating itself. In this sense we could say that $m_p/m_c$ is 1837 just because we are here. Other universes do exist as well, but nobody is around to see them. I am describing this somewhat paradoxical mechanism just in order to warn that we may expect quite exotic criteria to come into play in fixing the fundamental constants.

Coming back to Feynman graphs, there are a few properties of them worth quoting. In order to describe them I shall introduce the concept of monodromy group and of its ring. The monodromy group is a linear representation of the fundamental group which is particularly convenient in describing the branching properties of a Feynman amplitude.

The underlying idea is that although a multivalued function of the kind encountered here has infinitely many Riemann sheets it may happen that these values form a linear space of finite dimension $K$. A typical example is the logarithm all determinations of the function $\log(z)$ are of the form $\overline{\log(z)} + 2\pi i N$ where $N$ is any integer and $\overline{\log(z)}$ is for example the principal value. Here we have infinitely many choices for $N$ but the corresponding linear space has dimension $K = 2$ and is spanned by $\overline{\log(z)}$ and $2\pi i$, If this is the case, then the fundamental group acts in a natural way on this linear space. Let in fact $f_1, \dots, f_K$ be a basis in $V$ and $g$ a generic element in $\pi_1$. By $gf_i$ we mean in the following the analytic continuation of $f_i$ along $g$. According to our assumptions then we have constants $\lambda_{ij}(g)$ such that:

$$g \cdot f_i = \sum_{j=1}^{K} \lambda_{ji} f_j(g) \qquad i = 1 \dots K .$$

It is clear that the matrix elements $\lambda_{ij}(g)$ give rise to a map $\pi_1 \xrightarrow{\mathfrak{L}} \mathrm{Hom}\,(V)$. The image $\mathfrak{L}(\pi_1)$ is then by definition the monodromy group. The linear span of $\mathfrak{L}(\pi_1)$ is then the monodromy ring $R$. There is much information attached to both monodromy group and ring and also to the particular way in which the group is contained in the ring. Besides $\mathfrak{L}(\pi_1)$ and $R$ we also consider the group ring $B$ of $\pi_1$, that is, the set of all formal finite linear combinations $\sum_i c_i g_i,\ g_i \in \pi_1$. We have examined in detail the structure of these objects in the case of the single loop Feynman graphs and of the self energy graphs. Our analysis has been at this stage carried out still in more generality than the one initiated by the group of Fotiadi, et al. in the sense that we have replaced the customary Feynman propagators by the Speer propagators of the form $(p^2 - m^2 - i\varepsilon)^\lambda$ where $\lambda$ is complex and generic. The ensuing analysis is no more complicated than the standard one and has the advantage of being ready for the Speer renormalization technique. Moreover, in this case it is easier to follow the role of each individual propagator in the global structure of the graph. I shall skip further detail of the investigation, I only mention a few interesting ideas and conjectures which have arisen from it. In order to describe them more efficiently I shall introduce the notion of local conditions. These describe the behaviour of the amplitude near a singularity. For example, if we approach in the box diagram the leading singularity

in the physical case, we find there a square root singularity. With the introduction of Speer parameters this conclusion is modified but we still find that locally the function can be expanded as:

$$f(z) = f_0(z) + z^\mu f_1(z)$$

$$f_0, f_1 \text{ regular at } z = 0$$

where $z$ is a local variable such that the singular hypersurface is represented as $z = 0$. We have suppressed the notation for remaining variables for simplicity. Let us consider the discontinuity operator $a = \mathfrak{L}(\alpha) - 1$ where $\alpha$ is an elementary loop around $z = 0$. We see immediately that $a^2 = (e^{2i\pi\mu} - 1)a = Aa$. We refer to this equation as a local condition. In fact the kind of information that it yields is strictly limited to a neighbourhood of the singularity $z = 0$.

A second kind of information depends on the fact that if $a^2 = Aa$, then $a/A$ is a sort of projection operator. It is possible to estimate the dimension of the subspace associated with this operator. We know that if the pinch associated with the singularity is simple, then this dimension is one as in the quoted case of the leading box diagram singularity. Other local conditions arise from the Cutkosky-Steinmann identities and they occur at the intersections of two Landau varieties. A list of these conditions can be completed and it takes the form $\mathfrak{L}(\gamma_i) = 0$ where $\gamma_i$ are elements in $B$. Let $J$ be the two-sided ideal of $B$ generated by these elements. It is evident that there are maps:

$$B \to B/J \to R\,.$$

What is true in practice is that $R$ is isomorphic to $B/J$. We have not been able to prove this interesting fact rigorously and in general. It corresponds to a very economical situation, local conditions (as symbolized by $J$) are glued together by the fundamental group. The natural problem is now whether this is true for any Feynman graph and whether it is true for an $S$-matrix theory. If so, then the construction of the monodromy group for the $S$-matrix would be greatly facilitated for the local conditions are the easiest ones to impose. We have of course to solve the problem of properly defining $\pi_1$ and of constructing it explicitly. This problem is difficult but not totally beyond our present possibilities, after all we know it already in detail for infinite classes of graphs.

The next question is then what to do with the monodromy group. If $L$ would be algebraic and $K$ finite, it has been shown that (see Plemelj and Nastold) there exist always a set of solutions (the Riemann class) having this prescribed group. These solutions form a linear space with coefficients in the ring of rational function of dimension precisely $K$.

This indeterminacy would seem to complicate matters even further. I am convinced instead that we need it in order to deal efficiently with spin and different coupling schemes. We know indeed that Feynman amplitudes sharing the same masses and graphs but with different coupling schemes and spins share the same Landau varieties and therefore the same fundamental group. It is also true that their local behaviour near a singularity is the same modulo perhaps an integer power of the local variables. It follows that they have the same monodromy group. It is my hope that these functions may be shown to be uniquely fixed by the detailed knowledge of their behaviour near a singular point and that in turn this behaviour will be fixed by the spin and couplings of the involved particles. This is of course another open problem and a natural question to ask. Last open question is the role of unitarity. This role is coupled to the observation of Chew that the $S$-matrix cannot be conceived simply as a perturbation expansion if all particles have to be regarded on the same footing and the question of elementarity avoided altogether. If this is the case, the singularities are intertwined in such a way that simple poles appear on one sheet and not on others and more complicated relations have been shown to hold for multiparticle cuts by Schwarz and others.

This intertwining of singularities has been repeatedly used as an argument against giving any weight to the detailed investigation of Feynman amplitudes for indeed if it occurs, it is then impossible to write locally the $S$-matrix as a sum of separate amplitudes as in perturbation theory. I rather think that the objection is not entirely relevant. *FRA* yields an increasing amount of technical information on scattering amplitudes and they suggest several interesting connections among the relevant objects in the theory (the groups $\pi_1$, $\mathfrak{L}(\pi_1)$ and the rings $B$, $R$) which could be extremely useful in building a future theory. Furthermore, it should not be inferred that these objects can be defined for *FRA* only and for this reason are of limited if any value. *FRA* are merely testing grounds and I feel that time is ripe for producing examples where some of these nontrivial features are present and which are clearly nonperturbative. I would summarize my attitude at this stage as one of cautious optimism for clearly the extension of the present techniques of Nastold and Plemelj from algebraic varieties to transcendental limiting cases will certainly be far from trivial when (if ever) it will be achieved.

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R. GATTO (*)

# High Energy Behaviour of Weak and Electromagnetic Interactions.

## 1. Introduction.

In this lecture I shall summarize some recent work carried out at CERN and at Padova on problems connected to the behaviour at high momenta of weak and of electromagnetic interactions. I shall first summarize some results on the leading divergences in weak interactions. Specifically we shall discuss the most divergent terms which arise from virtual emission and absorption of intermediate W-mesons and discuss the main aspects of the problem.

In a quark model such terms — which in a cut-off theory are proportional at each perturbation order $n$ to $(G\Lambda^2)^n$ — have the important property of being essentially mass terms. An important feature is the possibility of connecting them to the outstanding problem of the origin of the Cabibbo angle [1] [2] [3].

We shall summarize the relevant speculations related to this problem. A more general discussion of the leading terms can be carried out in the frame of current algebra. We shall discuss the problem in connection with the determination of the commutator algebra for the currents and for the other relevant local operators. The detailed examination of the structure of the leading terms will lead to a particular scheme of current algebra, to be called the algebra of compound fields (CFA), and to its extensions and generalizations. Implications of CFA will be analyzed and the essential role played by scale invariance emphasized. Broken scale invariance allows for an extension of CFA, called generalized CFA, which contains a definite specifications of ill-defined limits occurring in field-algebra.

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Generalized CFA is a set of commutation relations relating the currents, the local densities which break scale invariance and chiral $SU_3 \times SU_3$, their derivatives, and the energy momentum tensor. It leads to definite relations among asymptotic electroproduction and neutrinoproduction cross-sections.

The accepted version, at this time, of weak interaction theory is the so called V-A theory [4]. It differs from the original Fermi theory [5] essentially in the specific choice of the covariants, which are practically fixed by the requirements of locality and chirality. But in fact, even in its modern formulation, the theory has remained at what we may call a « semiclassical » level. Efforts to bring the theory of weak interactions to a level comparable to that of quantum electrodynamics — still a prototype, uncomplete as it may be, of a second-quantized theory — have been rather unsuccessful.

The theory of weak interactions, at the current stage, has not, in all these years, advanced greatly from the level of a « radiation theory » of the kind used years ago in describing interactions of atoms with electromagnetic radiations.

The main question can be formulated as follows: what is behind the description one has obtained of the lowest order phenomena? It may be that the theory, as it now stands, is in fact capable of describing higher order phenomena, but lack of mathematical techniques has prevented us so far from quantitatively investigating such problems. This is an attitude which has often been invoked and recently has received some impulse from work on non-linear interactions and summation of perturbation series [6]. Difficulties and ambiguities [7] of such an approach are known and more work will be required. On the other hand it may be that only by a combined approach including strong and electromagnetic interactions (and may be other unknown interactions) and for a specific form of such interactions one can reach the stage of a finite second-quantized theory.

The two possibilities we have mentioned are of course neither exclusive nor the only possible ones [8]. Discussing all the alternatives would however be only speculative. But one thing appears as certain: that even if the development of ingenuous formal techniques will be capable of making the whole question of infinities unessential, such that separate treatment of each interaction gives a finite theory (and we are very far from that) it still will be useful to speculate on the relations among the different interactions. One point at least suggests that such relations are essential: weak currents are built out of $SU_3$ currents and $SU_3$ is an approximate symmetry of strong interactions.

A full understading of the above points is perhaps still far from us. Dealing only with the leading divergences, which we shall do here, is certainly uncomplete and criticable.

However the leading divergences are important at least in two respects. First: let us suppose that the theory develops a natural cutoff at about the unitarity limit. Then the leading divergences could be suspected of giving rise to effects of «strong» magnitude. This may be welcome on one side but highly embarassing on the other. The resulting «effective strong interactions» could for instance be expected to violate known strong interactions rules. Modifications of the theory to avoid such a possibility have been thought of [9]. Second: there is a strong indication (and it will form an essential part of our discussion here) that the leading divergences lead to terms with transformation properties under the chiral generators similar to those that one has hypothesized [10], for the terms that break the chiral symmetry in the strong hamiltoniam. This alone suggests a number of ideas and speculations as to possible requirements on these terms [1] [2]. A general frame for such speculations will be presented and various possibilities will be analyzed.

.The main point of our discussion here will be a study of the leading divergences at all orders. We shall consider first a naive quark model and obtain the result we have already anticipated: the leading divergences can be renormalized by general mass counterterms [11] [12]. Subsequently we shall consider a different derivation of the same result relying on current algebra techniques [13]. It will turn out that a definite commutator scheme (to which we shall refer as to «compound field algebra») emerges such that the naive quark model results again hold. It is not surprising that the scheme has an interpretation in terms of compound Yang-Mills fields. The result appears interesting from the point of view of strong interaction theory and of electromagnetism. We shall discuss different limiting procedures on Yang-Mills field theory and examine the physical implications, particularly in view of the forthcoming electron-positron annihilation experiments at high energy. An important point emerges while discussing such limits. It is connected, in the field-theoretic formulation, to the ambiguous meaning of a product of local operators. The intrinsic difficulties in solving such ambiguities suggest a current-algebraic approach relying on the concept of broken scale invariance [14].

To this purpose we shall exploit a model, based on Wilson's proposal [14] of postulating only a small number of independent local fields of small dimension (in energy units). The model [15], to be specified later on in greater detail, assumes that there exist (among others) the following independent local operators: 1) the currents $j_\mu^\alpha$, where $\alpha$ is an index of

chiral $U(3) \otimes U(3)$; 2) the densities $u^\alpha$ transforming according to representations $(1+s_u, s_u, s_u)(-s_u, -s_u, -s_u-1) \oplus (-s_u, -s_u, -s_u-1) \cdot$ $\cdot (1+s_u, s_u, s_u)$ of $U(3) \otimes U(3)$ (the $U(3)$ representations are as usual characterized by a triple $(f_1, f_2, f_3)$); 3) the densities $w^A$ ($A$ = scalar or pseudoscalar) which belong to $(s_w, s_w, s_w)(-s_w, -s_w, -s_w) \oplus (-s_w, -s_w, -s_w)(s_w, s_w, s_w)$; 4) the traceless part of the energy momentum tensor $\theta_{\mu\nu}$. The breaking of $U(3) \otimes U(3)$ is specified by requiring that the operator $\theta_{00} - \varepsilon^A w^A - \varepsilon^\alpha u^\alpha$, where $\varepsilon^A$, and $\varepsilon^\alpha$ are symmetry breaking parameters, is an $U(3) \otimes U(3)$ singlet. When all $\varepsilon$'s vanish one obtains the «skeleton» theory, which is assumed to be $U(3) \otimes U(3)$ invariant and conformal invariant (that is invariant under the conformal group, which contains the Lorentz group as a subgroup). For $\varepsilon \to 0$ one obtains operators $j_\mu^{(0)\alpha}$, $u^{(0)\alpha}$, $w^{(0)A}$, $\theta_{\mu\nu}^{(0)}$ which transform according to certain finite dimensional representations of the conformal group and together with these derivatives are the only operators of dimension less or equal than 4 (in energy units). Finally in the model we assume a regular dependence of the equal time commutator from the parameters $\varepsilon$. From the above general characterization of the model one obtains a set of commutation relations among the postulated fields and their derivatives. Such commutation relations can be regarded as encompassing a definite limiting procedure of the type required to obtain the « compound-field-algebra », but allowing for more generality. Observable physical consequences include asymptotic relations among asymptotic electroproduction cross-sections and neutrino cross-sections. Broken scale invariance seems thus to provide us with an extraordinary powerful tool to derive field theoretic results bypassing the ambiguities and complications that result from a rigorous analysis of current commutation relations [16].

## 2. Second semiweak order.

The matrix element of the second order virtual $W$ process of fig. 1 is

$$<\alpha|M|\beta> = -ig^2 \int \frac{d^4q}{q^2 - M^2}\left(g_{\mu\nu} - \frac{q_\mu q_\nu}{M^2}\right)\int d^4x\, e^{iqx} \tag{1}$$
$$<\alpha|[T(j_\mu^c(x)j_\nu^{c*}(0) + j_\mu^{c*}(x)j_\nu^c(0))]|\beta>.$$

It contains quadratic, logarithmic, and finite terms. Here $g$ is the semiweak coupling, $M$ the $W$-mass, and $j^c$ the Cabibbo current. It is understood that a vacuum to vacuum transition is subtracted from Eq. (1), corresponding to disconnected diagrams.

The extraction of the quadratic divergent part in Eq. (1) requires a repeated partial integration on space-time and the assumption of the

validity of a Johnson-Low-Bjorken limit [17] [18] for the matrix element of the operator

(2) $$\int d^4x e^{-iqx} T(D_c^*(0) D_c^*(x) + D_c(0) D_c(x))$$

where $D_c(x) = \partial_\mu j_\mu^c(x)$. Schwinger terms will not affect the result. This follows from general covariance considerations that will not be touched upon in this talk. If Schwinger terms are c-numbers, their irrelevance is

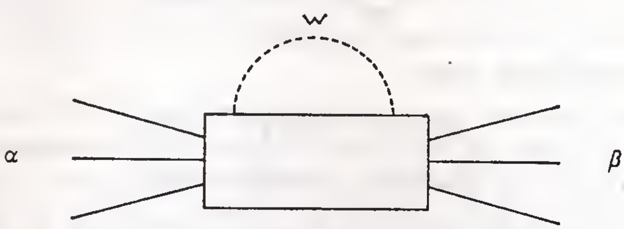


Fig. 1.

elementarily deduced from the subtraction of the disconnected diagrams that we have already mentioned. The leading divergent terms are of the form

(3) $$i\{[D_c(0), Q_c^*(0)] + [D_c^*(0), Q_c(0)]\} \frac{g^2}{M^2} \int \frac{d^4q}{q^2}$$

and are seen to be related to the charge-divergence commutator for the weak current. To evaluate it one needs the expression for the chiral symmetry breaking in the strong hamiltonian. The simplest assumption for such term is

(4) $$H' = \sum_l \varepsilon_l u_l(x)$$

where $u_l$ (together with pseudoscalar densities $v_l$) belong to $(3,\bar{3}) \oplus (\bar{3},3)$ ($l, i, j, \ldots$ are $SU_3$ indices) [10]. The divergences of the vector and axial $SU(3) \otimes SU(3)$ currents are formally obtained as

(5) $$D_i(x) = -\varepsilon_j f_{ijk} u_k(x)$$
$$D_i^5(x) = \varepsilon_j d_{ijk} v_k(x)$$

and the chiral $V$-$A$ divergences

(6) $$D_i = D_i + D_i^5$$

are

(7) $$D_i = -\varepsilon_j (f_{ijk} u_k - d_{ijk} v_k) .$$

It will be important to study the algebraic structure of the commutators between chiral charges and chiral currents. To this purpose we introduce operators [11]

$$E_j = -i\sqrt{\frac{2}{3}}\,[Q_0, D_i]$$

where $Q_0 = F_0 + F_0^5$, in terms of the chiral generator, $F_i$ and $F_i^5$. One has

$$E_i = \sum_l \varepsilon_l(-f_{lij}v_j + d_{lij}u_j) \tag{8}$$

and the commutation rules

$$\begin{aligned}[Q_i, D_j] &= if_{ijk}D_k + id_{ijk}E_k\\ [Q_i, E_j] &= -id_{ijk}D_k + if_{ijk}E_k\end{aligned} \tag{9}$$

The currents and divergences encountered before, see eq. (3), are related to those defined here by a Cabibbo rotation. On the charges the rotation is

$$Q'_k = e^{2i\theta F_7}Q_k e^{-2i\theta F_7}$$

and similar ones for the other quantities. One finds, in tensor notation

$$\begin{aligned}&[Q'_+, D'_+] = [Q'_-, D'_-] = 0\\ &[Q'_3, D'_3] = \frac{i}{\sqrt{3}}(\sqrt{2}\,E'_0 + E'_8)\\ &[Q'_\pm, D'_\mp] = \pm D'_3 + \frac{i}{\sqrt{3}}(\sqrt{2}\,E'_0 + E'_8)\\ &[Q'_\pm, D'_3] = \mp D'_\pm ; [Q'_3, D'_\pm] = \pm D'_\pm\\ &\left[Q'_\pm, \frac{i}{\sqrt{3}}(\sqrt{2}\,E'_0 + E'_8)\right] = D'_\pm\\ &\left[Q'_3, \frac{i}{\sqrt{3}}(\sqrt{2}\,E'_0 + E'_8)\right] = D'_3 .\end{aligned} \tag{10}$$

In particular

$$[Q'_+, D'_-] + [Q'_-, D'_+] = \frac{2i}{\sqrt{3}}(\sqrt{2}\,E'_0 + E'_8) \tag{11}$$

and from eq. (10)

$$\sqrt{2}\,E'_0 + E'_8 = b_0u_0 + b_3u_3 + b_8u_8 + b_6u_6 + b_7v_7 . \tag{12}$$

The properties of the algebra as given in eq. (10) are essential ingredients for discussing the higher orders [11]. For a breaking [10)

$$H' = \varepsilon_0 u_0 + \varepsilon_8 u_8 + \varepsilon_3 u_3 \tag{13}$$

one has in particular

$$b_3 = \frac{1}{\sqrt{3}} (\sqrt{2}\, \varepsilon_0 + \varepsilon_8) \sin^2 \theta + \varepsilon_3 \cos^2 \theta \tag{14}$$

$$b_8 = \frac{1}{3} (\sqrt{2}\, \varepsilon_0 + \varepsilon_8) (2 - 3 \sin^2 \theta) + 2\varepsilon_8 \sin^2 \theta + \frac{1}{\sqrt{3}} \varepsilon_3 \sin^2 \theta\,. \tag{15}$$

The terms proportional to $u_6$ and $u_7$ in eq. (12) are proportional to current divergences. They are thus uneffective in producing transitions. Concerning $u_0$ one can argue that its presence is not disturbing since it gives only a common mass shift to the particles of an $SU_3$ multiplet. Now, empirically, the *symmetry* of the solutions is in fact close to $SU_3$ and does not seem to bear much reminiscence of the original $SU_3 \times SU_3$. A combination of induced and spontaneous breaking is apparently effective at this stage. Therefore the understanding of $u_0$ appears to be at different level: it is connected with the appearence of $SU_3$ in the solution of the field equations.

The conditions $b_3 = 0$, $b_8 = 0$ were interpreted in ref. (1) as conditions on the Cabibbo angle and on $\varepsilon_3$.

One finds:

$$\mathrm{tg}^2\, \theta \cong \frac{\varrho}{3} \left(1 - \frac{\varrho}{6}\right) \tag{16}$$

$$\frac{\sqrt{3}\, \varepsilon_3}{\varepsilon_8} \cong \frac{1}{6} \varrho^2 \tag{17}$$

where

$$\varrho = -\left(1 + \frac{\sqrt{2}\, \varepsilon_0}{\varepsilon_8}\right).$$

In ref. (1) we followed a method based on the work of Glashow and Weinberg [19] to determine $\varrho$; an equivalent method is that of Gell-Mann, Oakes and Renner [20], who have carried out a complete and illuminating discussion of the breaking of $SU_3 \otimes SU_3$.

The results are: $\varrho = 0.15$ with the first method and $\varrho = 0.115$ with the latter. Such numbers are certainly affected by theoretical errors, very hard to estimate. If however one takes them as they stand one finds: for $\varrho = 0.15$, $\mathrm{tg}\, \theta = 0.22$; for $\varrho = 0.115$, $\mathrm{tg}\, \theta = 0.19$. The agreement is sur-

prising (and we hope not simply deceiving). For $\varepsilon_3$ one finds: $\sqrt{3}\,\varepsilon_3/\varepsilon_8 = 0.38 \times 10^{-2}$ for $\varrho = 0.15$ and $= 0.22 \times 10^{-2}$ for $\varrho = 0.115$. We recall for comparison that $\alpha \equiv e^2 \cong 0.72 \times 10^{-2}$.

It will be instructive to use symbolic quark masses ($p$, $n$, $\lambda$) in place of the $\varepsilon$'s. The expressions are

$$p = \sqrt{2}\left(\varrho - \sqrt{\frac{3}{2}}\,\varepsilon_3\right) \tag{18}$$

$$n = \sqrt{2}\left(\varrho + \sqrt{\frac{3}{2}}\,\varepsilon_3\right)$$

$$\lambda = \sqrt{2}\,(3 - 2\varrho)\,.$$

### 3. All orders in a free quark model.

The quark model that will be considered here contains fractionally charged quarks and a charged $W$ coupled to the Cabibbo current formed out of the quarks. It is the simplest model containing the relevant features for the problem at hand.

Fig. 2.

For a first insight consider the second order result [1]. In the model of this section the leading divergences in the mass shifts follow immediately from the graph in fig. 2 and are given, simply by taking into account the possible intermediate state, by

$$\delta m_p \propto m_p \cos^2\theta + m_p \sin^2\theta = m_p \tag{19}$$

$$\delta m_n \propto m_n \cos^2\theta$$

$$\delta m_\lambda \propto m_\lambda \sin^2\theta\,.$$

Requiring $\delta m_n - \delta m_\lambda = 0$ gives

$$m_n \cos^2\theta = m_\lambda \sin^2\theta \tag{20}$$

or

$$\mathrm{tg}^2\,\theta = \frac{m_n}{m_\lambda}. \tag{21}$$

Requiring $\delta m_\lambda - \frac{1}{2}(\delta m_p + \delta m_n) = 0$ gives

$$\frac{1}{p} = \frac{1}{n} + \frac{1}{\lambda}. \tag{22}$$

By use of eq. (19) one has regained eqs. (16) and (17). It is instructive to consider the fourth order. The proof would follow quite similarly, giving again eq. (19), except for graphs of the type in fig. 3. These graphs are strictly improper graphs when the intermediate particle is $n$, but they are proper graphs when such particle is $\lambda$. This detail destroys the symmetry (proper $\theta$ structure) following from simultaneous appearance in the current of $n$ and $\lambda$ with coefficients $\cos\theta$ and $\sin\theta$ respectively. We shall proceed as follows [11]. We define $\Sigma(K)$ as the contribution from the second order graph of fig. 2

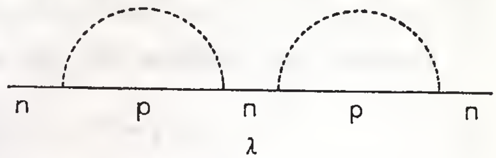


Fig. 3.

$$\Sigma(K) = \begin{bmatrix} f_2\gamma K\,\dfrac{1+i\gamma_5}{2} & 0 & 0 \\ 0 & f_2\gamma K\,\dfrac{1+i\gamma_5}{2}\cos^2\theta & f_2\gamma K\,\dfrac{1+i\gamma_5}{2}\cos\theta\sin\theta \\ 0 & f_2\gamma K\,\dfrac{1+i\gamma_5}{2}\cos\theta\sin\theta & f_2\gamma K\,\dfrac{1+i\gamma_5}{2}\sin^2\theta \end{bmatrix}$$

where $f_2$ is quadratically divergent in the cut-off. We add a counterterm

$$C = -\left(\sqrt{1-f_2}-1\right)E \tag{24}$$

where $E$ is defined by

$$\psi E\psi = [Q_{c'}, D_c^*(0)] + [Q_{c'}^*, D_c(0)] \tag{25}$$

$\psi$ being the quark triplet. The location of the poles (physical masses) is given by the zeros of

$$\det S^{-1} = \det(\gamma K - M - \Sigma + C) = 0\,. \tag{26}$$

It is easy to see although rather lenghty, that the poles are indeed at $m_p$, $m_n$, and $m_\lambda$.

The extension to any order [11] is now clear.

Consider the strictly proper graphs at order $r$ and call $\Sigma_r$ their sum. We also define

$$\Sigma^{(n)} = \Sigma_2 + \Sigma_4 + \dots \Sigma_{2n}\,. \tag{27}$$

These graphs have proper $\theta$-structure. $\Sigma^{(n)}$ is thus of the form in eq. (23) provided $F_n$ is substituted for $f_2$. Here

$$F_n = f_2 + f_4 + \dots + f_{2n}\,. \tag{28}$$

One only has to choose the new counterterm as

$$C_n = (1 - \sqrt{1 - F_n})E\,. \tag{29}$$

In fact we had already found that the pole location was independent of $f_2$.

Let us now consider the vertex corrections. We define a matrix $S$ by

$$\psi' = S\psi$$

where $\psi$ is the «physical» triplet. $S$ has to satisfy

$$\bar{\psi}[\gamma K - M - \Sigma + (1 - \sqrt{1 - F})E]\psi = \bar{\psi}'(\gamma K - M)\psi'\,. \tag{30}$$

One finds

$$S = 1 - (1 - \sqrt{1 - F})\frac{1 + i\gamma_5}{2}\begin{bmatrix}\cos^2\theta & \sin\theta\cos\theta \\ \sin\theta\cos\theta & \sin^2\theta\end{bmatrix} \tag{31}$$

and one readily verifies that

$$\frac{1 + i\gamma_5}{2}[\cos\theta n' + \sin\theta\lambda'] = \frac{1 + i\gamma_5}{2}\sqrt{1 - F}\,[\cos\theta n + \sin\theta\lambda]\,. \tag{32}$$

That is, $S$ leaves the Cabibbo direction invariant.

## 4. Current algebra calculation at fourth order.

The fourth-order matrix element is given by the operator

$$M_4 = \frac{g^4}{M^4}\int\frac{d^4q}{q^2}\frac{d^4K}{K^2}\,q_\mu q_\nu K_\alpha K_\beta\int e^{iqx + iK(y-z)}T(j_\mu^*(x)j_\alpha^*(y)j_\beta^-(z)j_\nu^-(0)) \tag{33}$$

which can be represented by means of the graph (0) in fig. 4.

As usual disconnected diagrams have to be subtracted. We shall use the commutators of field algebra [21]. The extraction of the leading

divergent terms can be performed with the help of a graphical procedure, that is developed in detail for instance in ref. (22). The procedure is essential to deal with the higher orders. Essentially one has to « reduce » each of the momenta $q_\mu$, $q_\nu$, $K_\alpha$, $K_\beta$, appearing in eq. (33). For instance, (but the procedure is not always so simple), for $q_\mu$ in eq. (33) this corresponds to writing $q_\mu e^{iqx} = -i(\partial/\partial x_\mu)e^{iqx}$ and then acting with $\partial/\partial x_\mu$ on the T-product by partial integration.

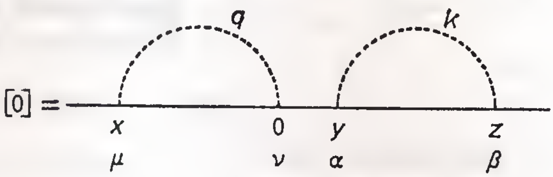


Fig. 4.

By this one gets a term with $(\partial/\partial x_\mu)j^*_\mu(x)$ substituted for $j^*_\mu(x)$ in the T-product and additional terms containing equal time-commutators. All such terms are graphycally represented in fig. 5.

The graph [3] vanishes because it is given by an integral odd in q. Next one operates with $(K_\alpha \rightarrow)$ on [1] obtaining [1,1], [1, 2], and [1, 3]. Then with $(q_\nu \rightarrow)$ on [1, 1], etc. (The detailed procedure can be found in reference (22). The procedure is rather lenghty and leads finally to the graphs in fig. 6, on which no further reductions can be made either because all momenta have been applied or because the technique is no further extendible in the same form.

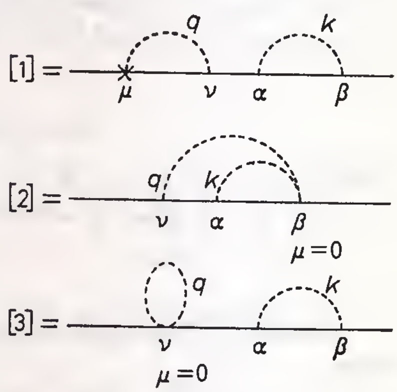


Fig. 5.

Clearly on [1, 1, 2, 2] and [1, 3, 2, 2] one has applied all momenta and performed all the indicated partial integrations. On the other hand [2, 2] and [1, 3, 3] have not been fully reduced. A different technique, more elaborate, has to be devised. The point is the following. Consider for instance [2, 2]. The total momentum transferred at the first vertex is $q + K$. Therefore the exponential associated is $e^{i(q+K)x}$. One has not made use of $(K_\alpha \rightarrow)$ and $(K_\beta \rightarrow)$; but the partial integration technique does not work for both since the derivative of the exponential is rather proportional to $(q + K)$. The technique to be used here consists of separate treatment of the longi-

tudinal and transverse components of $K_\alpha$ (and $K_\beta$) with respect to $p + q$. The reductions get very lenghty and involved and for the details we refer to ref. (22). The formal reduction leads to a result of physical interest: the appearance in the result of new commutators of the curl of the current with the current itself.

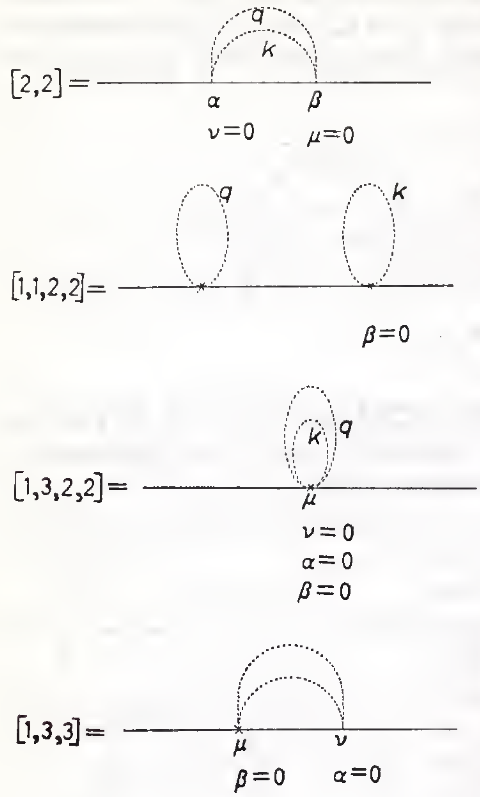

Fig. 6.

The diagrams of the type [1, 3, 2, 2] are clearly of the type

$$\{[Q^+, D^-] + + [Q^-, D^+]\} \int \frac{d^4q d^4K}{q^2 K^2} \tag{34}$$

and

$$\{[Q^3[Q^-, D^+(0)]] - - [Q^3[Q^+, D^-(0)]]\} \int \frac{d^4q d^4K}{q^2 K^2} . \tag{35}$$

From the algebra of currents and divergences summarized in eq. (10) one verifies that all such divergences are proportional to the combination

$$\sqrt{2}\, E_0 + E_8 . \tag{36}$$

Graphs of the type [1, 1, 2, 2] will clearly give integrals of the type

$$\int \frac{d^4q d^4K}{q^2 K^2} \int d^4x T\{[Q^-, D^+(x)]\,[Q^-, D^+(0)] + [Q^+, D^-(x)]\,[Q^+, D^-(0)]\} .$$

The « anomalous » graphs [1, 3, 3] can be shown, by the technique we have mentioned to give rise to terms of the same type. The graphs [2,2] are at the origin of new commutators. They give rise to leading divergences proportional to

$$\delta(x_0) \left[ \frac{\partial j_0}{\partial x_i} - \frac{\partial j_i}{\partial x_0} , j_l \right] . \tag{37}$$

## 5. Extended field algebra.

In the field algebra of Lee, Weinberg and Zumino [21] the weak currents are identified with gauge fields $\Phi'_\mu = \frac{m_0^2}{g^0} \Phi^0_\mu$, satisfying field equations ($a$ is the internal symmetry index)

(38) $$m_0^2 \Phi'_{a\nu} = \frac{\partial}{\partial x_\mu} F_{a\mu\nu} + g_0 J_{a\nu}$$

where

(39) $$F_{a\mu\nu} = \partial_\mu \Phi'_{a\nu} - \partial_\nu \Phi'_{a\mu} + g_0 C_{abc} \Phi'_{b\mu} \Phi'_{c\nu}$$

and

(39′) $$J_{a\nu} = F_{b\nu\mu} C_{abc} \Phi'_{c\mu} + \frac{\partial L'}{\partial(D_\nu \psi)} T_a \psi \,.$$

In the above equations $C_{abc}$ is the matrix of the structure constants, $L'$ is the part of the lagrangian depending on the matter field $\psi$, $T_a$ represents the algebra on the representation to which $\psi$ belongs, and $D_\nu$ are covariant derivatives in the sense of Yang and Mills. The commutation relations are

(40) $$\delta(x_0)\,[\Phi'_{ai}(x), \Phi'_{bj}(0)] = 0$$

(41) $$\delta(x_0)\,[\Phi'_{a4}(x), \Phi'_{bi}(0)] = - C_{abc} \Phi'_{ci}(0) \delta(x) - \frac{Z_0}{Z} \left(\frac{m}{g}\right)^2 \delta_{ab} \frac{\partial}{\partial x_i} \delta(x) \,,$$

(42) $$\delta(x_0)\,[\partial_4 \Phi'_{aj}(x) + \partial_j \Phi'_{a4}(x), \Phi'_{bi}(0)] = - \frac{1}{Z} m^2 \left(\frac{m}{g}\right)^2 \delta_{ab} \delta_{ij} \delta(x) + \\ + C_{abc} \Phi'_{cj}(0) \frac{\partial}{\partial x_i} \delta(x) - \left(\frac{g}{m}\right)^2 \frac{Z}{Z_0} C_{adc} C_{bde} \Phi'_{cj}(0) \Phi'_{ei}(0) \delta(x) \,,$$

(43) $$\delta(x_0)\,[\Phi'_{a4}(x), \Phi'_{b4}(0)] = i C_{abc} \Phi'_{c4}(0) \delta(x) \,.$$

We have used the notation

(44) $$Z = m^2 \left(\frac{m}{g}\right)^2 \left(\frac{g_0}{m_0}\right)^2 \frac{1}{m_0^2}$$

(45) $$Z_0 = \frac{m^2}{m_0^2}$$

for the renormalization constants. In addition to the currents our set of field quantities includes the $u$'s and $v$'s. A consistent way of including such operators is to introduce independent canonical fields $s$ and $p$, of scalar and pseudoscalar character, such that

$$s_i = u_i - \langle u_i \rangle_0 \tag{46}$$

$$p_i = v_i \, . \tag{47}$$

By construction of an explicit lagrangian, including the symmetry breaking in the postulated form of eq. (13), one can verify that the canonical rules for $s_i$ and $p_i$ are in fact consistent.

The extension of field algebra (to be abbreviated as F. A.) obtained in this way will be called extended field algebra (to be abbreviated as E.F.A.) This is the algebraic frame in which we work.

By a straightforward, although rather lengthy, counting argument one can show, for the fourth order term discussed in this section, that the introduction of a counterterm proportional to

$$\sqrt{2}\, E_0 + E_8$$

in fact takes into account *all* those divergences. The terms proportional to the commutator in eq. (37) spoil such result. It is therefore important to establish under what conditions the physically important situation of leading divergences again behaving as terms of $(3,\bar{3}) \oplus (\bar{3},3)$ (as for example in the quark model of the previous section) again obtains.

In the commutator in eq. (42) the term on the right-hand-side containing a product of two fields $\Phi'$ is known to be responsible for the infinities in the electromagnetic mass differences.

This term is very badly defined since it contains a product of two fields taken at the same space-time point. In a limit $Z/Z_0 \to 0$ such term may vanish. In this case the electromagnetic mass differences would be finite [23]. Of course, to have finite electromagnetic mass differences, it would be sufficient that in the limit the unpleasant term be a c-number or a singlet under $SU_3$, for instance (This point will be discussed later on in more detail). Also one should note that the limit $Z/Z_0 \to 0$ does not automatically imply the vanishing of the expression, just because the remaining factor containing a product of two field operators is in general divergent. Thus the possibility of obtaining finite electromagnetic mass differences, requires an assumption about such a limit.

## LIMITS OF FIELD ALGEBRA.

### 6. Compound field Algebra.

We shall assume that a meaningful and compatible set of current commutators is obtained in the limit

$$\left(\frac{m_0^2}{g_0^2}\right) \to \infty \qquad \left(\frac{m_0^2}{g_0}\right)^2 m_0^2 \to \infty \,. \tag{48}$$

In this limit

$$\frac{Z}{Z_0} \to 0 \qquad Z \to 0 \,. \tag{49}$$

The unsubtracted Feynman propagator $\Delta'_{\mu\nu}(q^2)_F$ of the gauge particles is divergent

$$\Delta'_{\mu\nu}(0)_F = \infty \,.$$

In the commutation relation $[j_0(x), j_i(0)]\delta(x)$ (see eq. 41), the Schwinger term, proportional to $\frac{Z_0}{Z}$, is infinite; also infinite is the c-number term in the commutation relation $[\partial_0 j_i(x) - \partial_i j_0(x), j_k(0)]\delta(x_0)$ (see eq. 42). The last term in the expression for the latter commutator (see eq. 4) has a vanishing factor $\frac{Z}{Z_0}$ in front. It will be assumed that in limit this term is a c-number (later on we shall consider the possibility of adding a unitary singlet). We shall refer to the set of the commutation relations obtained in the limit as to «compound field algebra», abbreviated as CFA. The reference to compound fields is connected to the vanishing of the renormalization constants in the limit, as in eq. (49). In CFA all the leading divergences of weak interactions are proportional to commutators of charge and currents. An important point to be noted is that field algebra in the limit $Z/Z_0 \to 0$ and $Z \to 0$ does not satisfy the Jacobi identity. To verify this one has simply to apply the Jacobi identity to $[\Phi_0^\alpha(x)\,[\dot{\Phi}_i^\beta(y), \Phi_j^\gamma(z)]]\delta(y_0 - z_0)\delta(x_0 - y_0)$.

The equal time commutator $[\dot{\Phi}_i, \Phi_j]$ has (before the limit) a term proportional to $Z/Z_0$. Such a term commuted again with $\Phi_0$ gives some terms independent of $Z$ and $Z_0$, because of the inverse factor $Z_0/Z$ appearing in the last term of eq. (41). On the other hand the Jacobi identity holds (before the limit). But then it cannot hold in the limit because the term we have discussed will not be there if the limit is performed first (the

equal time commutators $[\dot{\Phi}_i[\Phi_j, \Phi_0]]$ and $[\Phi_j[\Phi_0, \dot{\Phi}_i]]$ do not contain any finite term from cancellation of $Z/Z_0$ with $Z_0/Z$).

The non-validity of the Jacobi identity makes it necessary to formulate proofs by first calculating the leading divergences outside the limit and only afterwards performing the limit to CFA. The argument develops quite easily at 4-th order, taking advantage of the results in section 4. However the proof under such conditions becomes extremely complicated at the higher orders. We will not reproduce it here but refer to ref. (22).

## 7. CFA and leading weak divergences.

By a simple combinatorial argument that will not be reproduced here (see ref. (22)) one can show from our fourth order results that for CFA (enlarged to « extended compound field algebra », ECFA, to include the densities $u$ and $v$) one has the result that a counterterm proportional to $\sqrt{2}\, E_0 + E_8$ renormalizes the leading divergences of the theory. By a complex proof in EFA and then in the limit of ECFA one can show that the same results hold at all orders [24]. We have already mentioned some of the qualifications to be made before enunciating such a result. Also in the higher order result they are all connected with the question of proper definition of field products at same space time point. Nevertheless it is astonishing how the formal proof goes through in spite of its great algebraic complexity and apparently suggests that the result has a definite validity. On the other hand the result is consistent with that obtained in the quark model.

We have based all our discussion on the strong symmetry breaking of the form

$$H'(x) = \sum_l \varepsilon_l u_l(x) \,. \tag{50}$$

The result for the leading divergences is that they are all accounted for (in the quark model or more generally with the commutators of (CFA) by a general counterterm

$$F(\sqrt{2}\, E_0 + E_8) = F(b_0 u_0 + b_8 u_8 + b_3 u_3 + b_6 u_6 + b_7 b_7) \,. \tag{51}$$

In eq. (51) $F$ is unknown but $b_0$, $b_8$, $b_3$, $b_6$ and $b_7$ are all obtained directly from the coefficients of the algebra of chiral charges and chiral divergences in the rotated Cabibbo frame. Differently said, $b_0 - b_7$ are the same one calculates at lowest order. The point arises whether such a priori unexpected simplification in the problem of weak infinities also

holds for other forms of $H'$, for instance by also adding terms transforming as $(1,8) \oplus (8,1)$. The answer is negative. In a general theoretical frame, where one likes to consider together weak electromagnetic and strong interactions, such an answer appears as an argument in favor of the choice $(3,\bar{3}) \oplus (\bar{3},3)$ for the terms breaking the chiral symmetry.

In addition to the result we have just indicated, an interesting corollary is the following: not only at second order [25], but actually at any order, for the models we have considered one has absence of leading divergences in transitions which violate strangeness and/or parity. In particular non-leptonic decays are free of leading divergences.

## 8. CFA and electron-positron annihilation into hadrons. Sum rules.

It is well known [26] [27] that the total cross section for $e^+e^-$ annihilation into a set of states $F$, in the one-photon approximation, can be related to the contribution from the intermediate states of $F$ to the absorptive part $\Pi$ of the photon propagator, or equivalently, to the spectral function $\varrho$ of the vacuum expectation value of the e. m. commutator.

Specifically, calling $\sigma_F(E)$ the total cross-section (at c. m. energy of each beam) for the (one-photon) annihilation

$$e^+ + e^- \to F \tag{52}$$

one has

$$\sigma_F(E) = \frac{\pi^2\alpha}{E^2}\,\Pi_F(-\,4E^2) \tag{53}$$

where $\Pi_F(K^2)$ is the contribution from $F$ to $\Pi(K^2)$, the absorptive part of the photon propagator. In terms of the spectral function $\varrho(\sigma^2)$ of the Lehman-Kallen representation

$$\langle[j_\mu^{em}(x), j_\nu^{em}(0)]\rangle_0 = i\int_0^\infty d\sigma^2\varrho(\sigma^2)\left(\delta_{\mu\nu} - \frac{1}{\sigma^2}\,\partial_\mu\partial_\nu\right)\Delta(x,\sigma^2) \tag{54}$$

one has

$$\sigma_F(E) = \frac{\pi^3\alpha^2}{E^4}\,\varrho_F(4E^2)\,. \tag{55}$$

In the early paper in ref. (26) it was pointed out that eqs. (53) or (55) could be used to try some educated guesses as to the asymptotic behaviour of $\sigma(E)$.

Here we shall define the Sugawara model as the limit in eq. (65) on the Yang-Mills Lagrangian. A straightforward conclusion is that the sum rule

$$\int d\sigma^2 \frac{\varrho(\sigma^2)}{\sigma^2} = C \frac{1}{m^2} \left(\frac{g}{m}\right)^2 \tag{66}$$

holds for the model. This is enough to establish, provided the physical mass $m$ is not zero, a behaviour $\varrho(\sigma^2) \to 0$ such as to make the integral convergent. For instance

$$\varrho(\sigma^2) \sim \frac{1}{\log^2(\sigma^2)} \, . \tag{67}$$

This alone implies that $\sigma(E)$ decreases faster than $E^{-4}$, for instance

$$\sigma(E) \sim \frac{1}{E^4} \frac{1}{\log^2 E} \tag{68}$$

such that (66) is satisfied. The difficulty we have already mentioned in connection with the bilinear term occurring in the right-hand-side of eq. (42) is particularly evident in the Sugawara model. If the vacuum expectation value of such term were to vanish one would have a sum rule

$$\int d\sigma^2 \varrho(\sigma^2) = 0 \tag{69}$$

in the limit, from which one would have to conclude that the model is self-contradictory. Indeed the c-number term in eq. (42) behaves like $Cm_0^2$ and vanishes in the limit. The vacuum expectation value of the bilinear term in the same commutator however diverges and makes the integral in eq. (69) infinite. So one has rather

$$\int d\sigma^2 \varrho(\sigma^2) = \infty \tag{70}$$

which implies that $\varrho(\sigma^2)$ does *not* decrease too fast to make the integral convergent. For instance $\varrho(\sigma^2)$ does *not* decrease as

$$\sigma(\sigma^2) \sim \frac{1}{\sigma^2} \frac{1}{(\log \sigma^2)} \tag{71}$$

or faster. This means that $\sigma(E)$ does *not* decrease as

$$\sigma(E) \sim \frac{1}{E^6} \frac{1}{\log^2 E} \tag{72}$$

or faster. Unfortunately, arguments based on scale invariance [14] *cannot* be applied to conclude that the divergence in eq. (70) is quadratic. The reason is obvious. The Sugawara limit leaves a finite Schwinger term in the commutator of a time component and a space component of a current and its coefficient has dimensions.

To see the point explicitly we note that scale invariance would lead to a divergent contribution to the integral in eq. (70), from the ill-defined vacuum expectation value of the operator product, increasing like the sixth power of an energy cut-off. The c-number contribution instead vanishes, as we have seen. Now such a highly divergent behaviour is clearly inconsistent with the convergence of the sum rule in eq. (66). Evidently scale invariance is unapplicable.

Scale invariance can be applied to CFA and gives the same conclusion one would obtain by (erroneously) neglecting the singular term in the commutator of the current with its curl. The c-number term contributes a quartic divergence and again a quartic divergence is contributed by the singular term. There is full consistency between a quartic divergence in $\int \varrho d\sigma^2$ and a quadratic divergence in $\int (\varrho/\sigma^2) d\sigma^2$, and this is in fact what we have called the « standard realization » of CFA. A limit $m_0 \to 0$ closely related to *CFA* is the minimal algebra of Bjorken and Brandt [31]. Here the c-number term contributes a finite piece to $\int \varrho d\sigma^2$ but a quartic divergence comes from the singular term, again on the basis of scale invariance. The fact that scale invariance does not apply to DFA or to the Sugawara model is in itself a consequence of the finiteness of $\int (\varrho/\sigma^2) d\sigma^2$ which brings a scale in these theories (the coefficient of the Schwinger term in the $[j_0, j_i]$ commutator is a dimensional parameter). This however does not happen in CFA or in the minimal algebra.

One can convince oneself from the preceding discussion that scale invariance, when applicable, leads in some cases directly to general conclusions, bypassing the difficulties and ambiguities of a field-theoretic calculation (by the dubious $\varepsilon$-limiting procedure or by Feynman graph calculations). To gain an extension of CFA and at the same time an implicit specification of the limiting procedure which it implicitly contains we shall in a later section resort to a formulation where (broken) scale invariance is an essential ingredient. The extension [15] has the main purpose to free CFA from restrictions that it would impose to asymptotic limits at infinite momentum of electroproduction cross-sections and neutrino-production cross-sections if treated without properly taking the limiting procedures in due account.

## An alternative approach.

9. – Here instead of following the renormalization approach we consider the possibility that the summed up leading weak divergences are finite or can be treated as finite.

We take

$$L = \overline{\psi}_0[-i\gamma\partial + M_0]\psi_0 + g_0\overline{\psi}_0\gamma_\mu W^\mu P_+ \Lambda(\theta_0)\psi_0 + \text{h. c.} \tag{73}$$

where

$$P_\pm = \frac{1}{2}(1 \pm i\gamma_5) \tag{74}$$

$$\Lambda(\theta_0) = \frac{1}{2}(\lambda_1 + i\lambda_2)\cos\theta_0 + \frac{1}{2}(\lambda_4 + i\lambda_5)\operatorname{sen}\theta_0 \tag{75}$$

$$M_0 = \begin{bmatrix} p_0 & & \\ & n_0 & \\ & & \lambda_0 \end{bmatrix}. \tag{76}$$

We perform a wave-function renormalization

$$\psi_0 = (Y_+P_+ + Y_-P_-)\psi \tag{77}$$

and rewrite $L$ as follows

$$L = L_0 + L_I \tag{78}$$

$$L_0 = \overline{\psi}(-i\gamma\partial + M)\psi \tag{79}$$

$$M = \begin{bmatrix} p & & \\ & n & \\ & & \lambda \end{bmatrix} \tag{80}$$

$$L_I = g\overline{\psi}\gamma_\mu W^\mu \Lambda(\theta)P_+\psi + C + \text{h. c.} \tag{81}$$

$$\begin{aligned} C = \overline{\psi}\{(-i\gamma\partial)(Y_+^*Y_+P_+ + Y_-^*Y_-P_- - 1) + (P_+Y_+^*M_0Y_- +\\ + P_-Y_-^*M_0Y_+ - M)\}\psi + \overline{\psi}\gamma_\mu W^\mu P_+(g_0Y_+^*\Lambda(\theta_0)Y_+ - g\Lambda(\theta))\psi\,. \end{aligned} \tag{82}$$

For the leading divergences we have a Ward identity relating, as usual, vertex and propagator. In fact the term corresponding to the divergence of the current is not a leading divergent term (because leading

divergences correspond to neglecting the internal masses, and such a term would thus be more convergent). We therefore require

$$g_0 Y_+^* \Lambda(\theta_0) Y_+ - g\Lambda(\theta) = 0 \tag{83}$$

(there is no need for vertex counterterms of different tensor character).

Next we require

$$S_F'^{-1}(p) = p\gamma - M\,. \tag{84}$$

Now $S_F'^{-1}(p)$ calculated from (78) and (83) is

$$S_F'^{-1}(p) = p\gamma - M - \Sigma(p) + C(p) \tag{85}$$

where

$$\Sigma(p) = -Fp\gamma P_+ A(\theta) \tag{86}$$

$$A(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos^2\theta & \sin\theta\cos\theta \\ 0 & \sin\theta\cos\theta & \sin^2\theta \end{bmatrix}. \tag{87}$$

From eqs. (84) and (85) one has

$$Y_-^* Y_- = 1 \tag{88}$$

$$Y_+^* Y_+ = 1 - FA(\theta) \tag{89}$$

(90) $Y_-^* M_0 Y_+ = M$ (and the hermitian conjugate equation $Y_+^* M_0 Y_- = M$).

If $Y_+$, $Y_-$ exists satisfying (83), (88), (89) and (90) one has succeded in reducing the original Lagrangian, eq. (73), to one where the leading weak divergences are compensated but the « physical » quarks have now physical masses as given from the matrix $M$ and are coupled with a different Cabibbo angle.

The construction of $Y_-$ and $Y_+$ and the relations between unrenormalized and renormalized quantities can be obtained by algebraic manipulations. We shall not give here the details which can be found in ref. (22). The relations one finally obtains between the renormalized and the unrenormalized quantities are (see ref. 22):

$$x^2 = \frac{p_0^2}{p^2} = \frac{n_0^2\lambda_0^2}{n^2\lambda^2} \tag{91}$$

$$n_0^2 + \lambda_0^2 = \frac{n_0^2\lambda_0^2}{n^2\lambda^2}(n^2c^2 + \lambda^2 s^2) + (n^2 s^2 + \lambda^2 c^2) \tag{92}$$

$$n^2 + \lambda^2 = \frac{n^2\lambda^2}{n_0^2\lambda_0^2}(n_0^2c_0^2 + \lambda_0^2s_0^2) + (n_0^2s_0^2 + \lambda_0^2c_0^2) \tag{93}$$

with the abbreviations $c = \cos\theta$, $s = \operatorname{sen}\theta$, $c_0 = \cos\theta_0$, $s_0 = \sin\theta_0$.

An alternative form for the set of eqs. (92) and (93) is

$$t^2 = \frac{n^2}{\lambda^2}\frac{\lambda_0^2 - \lambda^2}{n_0^2 - n^2}\frac{\lambda^2 - n_0^2}{\lambda_0^2 - n^2} \tag{94}$$

$$\frac{t_0^2}{t^2} = \frac{\lambda^2}{n^2}\frac{n_0^2}{\lambda_0^2}\frac{(\lambda_0^2 - n^2)^2}{(\lambda^2 - n_0^2)^2} \tag{95}$$

where $t = \operatorname{tg}\theta$ and $t_0 = \operatorname{tg}\theta_0$.

Let us first note that for $n_0^2 = n^2$ and $\lambda_0^2 = \lambda^2$ one would obtain $p = p_0$ from (91) and both (92) and (93) would be identically satisfied for any $\theta$ and for any $\theta_0$; (the same conclusion follows from $p_0^2 = p^2$ and $\lambda_0^2 = \lambda^2$; or $p_0^2 = p^2$ and $n_0^2 = n^2$).

In the approach developed in the previous sections a counterterm proportional to a fixed linear combination of the operators $u_0$, $u_6$, and $v_7$ was introduced. No particular conclusions can be drawn from the set of eqs. (91), (93) since, assuming $p$, $n$, $\lambda$ to be known, one still has four quantities $p_0$, $n_0$, $\lambda_0$ and $\theta_0$ completely unknown, in addition to $\theta$.

A counterterm proportional tu $u_0$ would require the condition $M = M_0 + \Delta \cdot 1$, that is $p_0 = p + \Delta$, $n_0 = n + \Delta$, and $\lambda_0 = \lambda + \Delta$. We shall first impose only the conditions $n_0 = n + \Delta$ and $\lambda_0 = \lambda + \Delta$, corresponding to slightly more general counterterm. Inserting $n_0 = n + \Delta$ and $\lambda_0 = \lambda + \Delta$ one has

$$t^2 = \frac{n^2}{\lambda^2}\frac{2\lambda + \Delta}{2n + \Delta}\frac{(\lambda - n) - \Delta}{(\lambda - n) + \Delta} \tag{96}$$

$$\frac{t_0^2}{t^2} = \left(\frac{\lambda}{n}\frac{n + \Delta}{\lambda + \Delta}\frac{(\lambda - n) + \Delta}{(\lambda - n) - \Delta}\right)^2 . \tag{97}$$

The result $\operatorname{tg}^2\theta = \frac{n}{\lambda}$ (see eq. 21) is recovered in this approach in the limit $\Delta \to 0$. In this limit one has

$$t^2 \to \frac{n}{\lambda} \tag{98}$$

$$\frac{t_0^2}{t^2} \to 1 . \tag{99}$$

Eq. (98) is the desired result and eq. (99) suggests $\theta_0 = \theta$. Therefore small $\Delta$ will give a very satisfactory situation.

Another interesting limit obtains if one instead requires $n_0 \to 0$ (i. e. $\Delta \to -n$). One has in this case $\lambda_0 \to \lambda - n$, and $p_0 \to 0$. The situation $n_0 = 0$, $p_0 = 0$ corresponds to an original chiral $SU_2 \times SU_2$ before adding weak interactions. For the angles one has

$$t^2 = \frac{n}{\lambda}\,\frac{2\lambda - n}{\lambda + 2n} = 2\,\frac{n}{\lambda} \tag{100}$$

since $(n/\lambda) << 1$. Also, in this case,

$$t_0^2 \to 0\,. \tag{101}$$

Eq. (100) does not lead to such a satisfactory determination of the Cabibbo angle as eq. (101), if one takes as final the determination of $n/\lambda$ from the values of $\varrho$ (see Section 2). From eqs. (18) one has

$$\frac{n}{\lambda} \simeq \frac{1}{3}\varrho\,.$$

A factor $\sqrt{2}$ in the value of tg would modify the two determinations of Section 2 into the values $\operatorname{tg}\theta = 0.27$ and $\operatorname{tg}\theta = 0.31$ respectively.

Although numerically perhaps less satisfactory than the result $t^2 = n/\lambda$, the possibility in eq. (100) still deserves some attention, also in view of the quite recognized possibility that the values of $\varrho$ (or of $c$) taken in section 2, are subject to large errors (a 40% error in the value of $\varrho$ would make eq. (100) compatible with experiment). The attractive feature of the solution $n_0 \to 0$, $p_0 \to 0$ is that such a limit corresponds to an exact $SU_2 \times SU_2$ for the unphysical particles. Besides one has in the limit $\theta_0 = 0$, as indicated from eq. (101). We note also that the alternative limit $\lambda_0 \to 0$ (i. e. $\Delta \to -\lambda$) gives $p_0 \to 0$, $n_0 \to n - \lambda$, leading again to eq. (100) but in this case $\theta_0 \to \pm\pi/2$.

If we try the full set of conditions, $p_0 = p + \Delta$, $n_0 = n + \Delta$, $\lambda_0 = \lambda + \Delta$, the value of $\Delta$ is determined from the values of $p$, $n$ and $\lambda$. A solution is $\Delta = \dfrac{n\lambda}{p} - \lambda - n$ giving

$$t^2 = \frac{n^2}{\lambda^2}\,\frac{2\lambda\left(1 + \frac{1}{2}\delta\right) - n}{\lambda\delta + n}\,\frac{\lambda(1-\delta)}{\lambda(1+\delta) - 2n} \tag{102}$$

where we have put

$$\frac{n}{p} = 1 + \delta\,.$$

It is interesting that for $\delta \to 0$ (i. e. exact $SU_2$ for the « physical » particles) one has $\Delta = -n$, thus recovering the solution in eqs. (100) and (101). One would have in this case: $n_0 \to 0$, $p_0 \to 0$ (i. e. $SU_2 \times SU_2$ for the « unphysical particles), $\theta_0 \to 0$, and $t^2 \cong 2(n/\lambda)$.

In the above discussion we have limited ourselves to considering some possibilities. Additional possibilities can be contemplated but we shall not try to make a complete discussion. The reader will recognize that the possibility $\Delta \to 0$, leading to eqs. (98) and (99), is closely related to the approach of the previous sections and the subsequent extension to higher orders whenever it happens that the summed up leading divergences give in fact a small contribution. In particular it practically coincides with the perturbative limit examined in Section 2. The possibility leading to eqs. (100) and (101), i. e. $\Delta \to -n$, is rather different. It has the interesting feature of corresponding to a limit $p_0 \to 0$, $n_0 \to 0$, (i. e. $SU_2 \times SU_2$ for the unphysical particles) and $\theta_0 \to 0$. It leads however to a value for the Cabibbo angle less acceptable unless the determination of the parameter $\varrho$ (or equivalently of $c$) from strong interactions is in error by some 40%. Finally the last of the possibilities considered, leading to eq. (102) with $\delta \to 0$, appears also of interest in that no $SU_2$ breaking has been introduced neither for physical particles nor for unphysical particles. Practically, the $SU_2$ input for unphysical particles leads here to exact $SU_2 \times SU_2$ for unphysical particles and to $\theta_0 \to 0$.

Again the Cabibbo angle so determined is only of the right magnitude and one should rely on the possibility of errors in $\varrho$, as mentioned above, or just admit that the explicit neglection of any $SU_2$ breaking in this case is responsible for the unaccuracy.

In conclusion we do not want to advocate the viewpoint that the discussion in this section stands on a better footing than the approach presented in the preceding sections, based on introducing a more complex counterterm. Both approaches cannot be claimed to be final. Our feeling however is that the results obtained, and possibly eq. (16), or eq. (21), in different notations are correct and that a nearer understanding of the problem may sooner or later be gained by more work on the subject.

10. – Before closing this section we can briefly comment on related work that has appeared recently in the literature. A full bibliography on the problem of divergences of weak interactions would have to be very long. We shall refer to the recent papers by: F. E. Low [32], N. Christ [33], T. D. Lee [34], M. Gell-Mann, M. L. Goldberger, N. M. Kroll [35] and F. E. Low, T. D. Lee and G. C. Wick [36], G. Segre [37], H. Terazawa [38],

L. I. Li and G. Segre [39], T. Appelquist and G. Carlson [40], R. N. Mohapatra and J. Subba Rao [41].

Recent methods based on special summation procedures (see G. Efimov [6], E. S. Fradkin [6], R. Delbourgo, A. Salam, and J. Strathdee [6], where additional references can be found) might turn to be useful for weak interactions.

Among previous work on weak divergences we note the peratization approach by G. Feinberg and A. Pais [42], and some particular calculations, such as for instance those of B. L. Ioffe and E. P. Shabalin [43] and of R. N. Mohapatra, J. Subba Rao, and R. E. Marshak [44]. On the subject of $SU_3 \times SU_3$ breaking in addition to the papers by S. Glashow and S. Weinberg [19] and by M. Gell-Mann, R. J. Oakes and B. Renner [20], there are many recent contributions. We refer to the review given by B. Renner at Lund [45].

On the subject of spontaneous breaking [46] [47] of $SU_3 \times SU_3$ we would like to mention the recent work by L. Michel and L. Radicati [48] (see also G. F. Cicogna, F. Strocchi, and R. Vergara-Caffarelli [49]).

Spontaneous breaking of $SU_3$ was treated, among others, by: R. Brout [50], N. Cabibbo [52], and L. Michel and L. Radicati [52].

As to the problem of the origin of the Cabibbo angle, there is an approach by Cabibbo and Maiani [2] [12] again making use of the idea of relating the angle $\theta$ to the weak self-masses. The formal developments are essentially identical to ours.

The physical interpretation is however different and rests on the requirement of a consistency condition to be satisfied by the different interactions and wich can be satisfied only if additional u-spin invariant contributions are included.

In a recent paper [53] Oakes has related the e.m. tadpole suggested from the theory to the $\eta \to 3\pi$ amplitudes. We would like to mention also the recent paper by Tanaka and Tarjanne [54] based on solving a set of linear equations for spontaneous breaking (see N. Cabibbo [51]). The modifications of the problem in the presence of neutral weak currents are considered, for special models, in the paper in ref. (1) and also by C. H. Albright [55].

## Generalized cfa.

11. – From a discussion of Lagrangian field theory one can abstract the possibility of a class of theories for which the generators of the conformal group (group of conformal spacetime transformations, including,

besides the inhomogeneous Lorentz transformations, also dilatations and special conformal transformations) can be written as

$$(103)\qquad P_\mu = \int d^3x\theta_{0\mu} \qquad M_{\mu\nu} = \int d^3x(x_\mu\theta_{0\nu} - x_\nu\theta_{0\mu})$$

$$(104)\qquad D = \int d^3x x^\mu\theta_{0\mu} \qquad K_\mu = \int d^3x(2x_\mu x^\sigma\theta_{0\sigma} - x^2\theta_{0\mu})$$

in terms of a divergenceless and symmetric energy momentum tensor $\theta_{\mu\nu}$. In such theories one has

$$(105)\qquad \dot{D} = \int d^3x\theta^\mu_\mu$$

$$(106)\qquad \dot{K}_\nu = \int d^3x 2x_\nu\theta^\mu_\mu$$

and from Lorentz invariance one infers that dilatation invariance $\dot{D} = 0$ requires also $\dot{K}_\gamma = 0$ (i.e. invariance under special conformal transformations). The model we shall discuss will be assumed to belong to such a class of theories.

We shall summarize its properties relevant to our discussion in a specific set of assumptions. The assumptions do not necessarily specify the model completely; however they are sufficient for deriving the commutator among some of its local operators, including the currents, the energy-momentum tensor, and the densities responsible for symmetry breaking. The assumptions are:

*A*) There exist the following linearly independent local operators:

1) The chiral currents $j^\alpha_\mu(x)$ (where $\alpha$ is an $U(3)\otimes U(3)$ index: $\alpha = (a, A)$, with $a = 0, ..., 8$, $A = +$ or $-$); the charges $Q^\alpha(x_0)$, defined as

$$Q^\alpha(x_0) = \int d^3x j^\alpha_0(x)\,,$$

generate at equal times a Lie algebra isomorphic to the Lie algebra of $U(3)\otimes U(3)$:

$$(107)\qquad [Q^\alpha(x_0), Q^\beta(x_0)] = iC^{\alpha\beta\gamma}Q^\gamma(x_0)\,.$$

2) The fields $u^\alpha(x)$, which transform as tensor of the irreducible representation $R^{(u)} \equiv (1 + s_u, s_u, s_u)(-s_u, -s_u, -1-s_u) \oplus (-s_u, -s_u, -s_u - 1)(1 + s_u, s_u, s_u)$ of the group $[U(3)\otimes U(3)]_{x_0}$ generated by the

charges $Q^\alpha(x_0)$ ($s_u$ is an integer). The representations of $U(3)$ are specified as usual by three integers $(f_1, f_2, f_3)$.

3) The fields $w^A(x)$, which transform as tensors of the irreducible representation $R^{(w)} \equiv (s_w, s_w, s_w)\,(-s_w, -s_w, -s_w) \oplus (-s_w, -s_w, -s_w) \cdot (s_w, s_w, s_w)$ of the group $[U(3) \otimes U(3)]_{x_0}$ ($s_w$ is a non-zero integer).

4) The traceless part of the energy momentum tensor $\theta_{\mu\nu}(x)$.

*B*) The operator $\theta_{00}(x) - \varepsilon^\alpha u^\alpha(x) - \varepsilon^A w^A(x)$ commutes with all charges $Q^\alpha(x_0)$. The dimensional constants $\varepsilon^\alpha$ and $\varepsilon^A$ are symmetry breaking parameters.

*C*) In the limit $\varepsilon^\alpha \to 0$, $\varepsilon^A \to 0$ one obtains the «skeleton» theory (in Wilson's nomenclature) which is invariant with respect to the transformations:

1) Of the $U(3) \otimes (3)$ group whose generators are the limits for $\varepsilon^\alpha \to 0$, $\varepsilon^A \to 0$ of the charges $Q^\alpha(x_0)$.

2) Of the conformal group $C$, whose generators are obtained as the limits for $\varepsilon^\alpha \to 0$, $\varepsilon^A \to 0$ of the charges associated to the currents:

$$\theta_{\mu\nu}(x)\,,\quad M_{\rho\mu\nu} \equiv x_\mu \theta_{\rho\nu}(x) - x_\nu \theta_{\rho\mu}(x)$$
$$D_\mu(x) \equiv x^\nu \theta_{\mu\nu}(x)\,,\qquad K_{\mu\nu}(x) = 2x_\nu x^\rho \theta_{\mu\rho}(x) - x^2 \theta_{\mu\nu}(x)\,. \tag{108}$$

In the following we shall denote with a superscript (0) the operators of the skeleton theory: $A^{(0)} = \lim\limits_{\varepsilon^A, \varepsilon^\alpha \to 0} A$, where $A$ is an operator.

*D*) In the skeleton theory the operators $w^{(0)A}(x)$, $u^{(0)\alpha}(x)$, $j_\mu^{(0)\alpha}(x)$, and $\theta_{\mu\nu}^{(0)\alpha}(x)$ transform covariantly with respect to the charges of the conformal group, as tensors of an irreducible finite dimensional representation with $K_\mu = 0$ (i. e. those representations which behave irreducibly under the homogeneous Lorentz group).

The only operators with scale dimensions $l \geq -4$ are

1) c-numbers, with $l = 0$;
2) $w^{(0)\alpha}(x)$; $l = -\Delta'$; $1 \leq \Delta' < 4$;
3) $u^{(0)\alpha}(x)$; $l = -\Delta$; $1 \leq \Delta < 4$;
4) $j_\mu^{(0)\alpha}(x)$; $l = -3$;
5) $\theta_{\mu\nu}^{(0)}(x)$; $l = -4$;
6) possible derivatives of the above operators provided their $l$ is $\geq -4$.

*E*) The explicit dependence on $\varepsilon^A$, $\varepsilon^\alpha$ of the equal time commutators is regular in the neighborhood of $\varepsilon^A = 0$, $\varepsilon^\alpha = 0$.

The model is essentially a specification of a model by Wilson [14]. Wilson's skeleton theory is assumed to be only scale invariant. The specification is made here that, because of the limitation to that class of theories for which scale invariance implies conformal invariance, in effect one has a fully conformally invariant skeleton theory. Also we deal with $U(3) \otimes U(3)$ rather than with $SU(3) \otimes SU(3)$. The skeleton theory is invariant under $U(3) \otimes U(3)$; the breaking in the hamiltonian is due to a term which is singlet under $SU(3) \otimes SU(3)$ and behaves according to a representation of the type $(s, s, s)(-s, -s, -s) \oplus (-s, -s, -s) \cdot (s, s, s)$ of $U(3) \otimes U(3)$, plus additional terms which break $SU(3) \otimes SU(3)$. There is no term in the hamiltonian breaking conformal invariance and singlet under $U(3) \otimes U(3)$. The assumption $\Delta, \Delta' < 4$ implies that the breaking of $U(3) \otimes U(3)$ is associated to a breaking of scale invariance. The assumption $\Delta, \Delta' \geq 1$ follows from the general Källen-Lehman representation. We note that the physical interpretation of the skeleton theory cannot be obtained from a smooth limit on the complete theory. A zero-mass particle has 2 independent states of polarizations for any spin value $S$, instead of the usual $2S + 1$ states for a massive particle. The definition of asymptotic states is impossible when no quantities with dimensions of a length are present. The singularity of the renormalized propagator at $p^2 = 0$ can be more complex than a single pole correspoding to a massless particle. Nevertheless there is no reason to suspect that assumption $E$ is untenable, and in fact most of the physical implications follow from such an assumption. The implications of the assumptions on the commutator algebra of the currents, the energy momentum tensor, and of the densities $u$ and $w$, can be deduced by sophisticated and lengthy formal methods. We shall not enter here into any detail and rather refer to the papers quoted in reference [15], especially to the second of the two. An important tool is the use of Wilson's operator product expansion [14].

One finds that the energy momentum tensor of the full theory satisfies

$$\theta_{\mu\mu}(x) = (4 - \Delta')\varepsilon^s w^s(x) + (4 - \Delta)\Sigma\varepsilon^\alpha u^\alpha(x) .$$

We also define a non-covariant $\tilde{\theta}_{\mu\nu}$ as follows: $\tilde{\theta}_{00}$ is defined by the assumption $B$: $\tilde{\theta}_{00} = \theta_{00}(x) - \varepsilon^s w^s - \Sigma\varepsilon^\alpha u^\alpha$; $\tilde{\theta}_{0i}$ is equal to $\theta_{0i}$, and $\tilde{\theta}_{ik} = \theta_{ik} - \dfrac{1}{3}(3 - \Delta')\varepsilon^s w^s \delta_{ik} - \dfrac{1}{3}(3 - \Delta)\Sigma\varepsilon^\alpha u^\alpha \delta_{ik}$. Thus $\tilde{\theta}_{\mu\mu} = 0$.

We report here the commutators we shall be interested in:

$$[Q^\alpha(t), \tilde{\theta}_{\mu\nu}(\vec{x}, t)] = 0 \tag{109}$$

$$[Q^\alpha(t), \partial_\mu j_\nu^\beta(\vec{x}, t) - \partial_\nu j_\mu^\beta(\vec{x}, t)] = -iC^{\alpha\beta\gamma}[\partial_\mu j_\nu(\vec{x}, t) - \partial_\nu j_\mu(\vec{x}, t)] \tag{110}$$

$$\begin{aligned}\delta(x_0)\,[j_i^\alpha(x), \partial_0 j_k^\beta(0) - \partial_k j_0^\beta(0)] &= \delta^4(x)\,\{\delta^{\alpha\beta}[\delta_{ik}c_1\tilde{\theta}_{jj}(0) + c_2\tilde{\theta}_{ik}(0)] + \\ &+ \delta_{ik}\delta^{\alpha\beta}\varepsilon^s w^s(0) + \delta_{ik}G^{\alpha\beta\gamma\delta}\varepsilon^\gamma u^\delta(0) + \delta_{ik}c^{\alpha\beta} + \ldots\} + \text{Schwinger terms}\end{aligned} \tag{111}$$

where $C^{\alpha\beta\gamma}$ are the structure constants of $SU_3 \times SU_3$; the dots in eq. (111) stand for derivative operators which do hot contribute between states of equal fourmomentum; $c_1$, $c_2$, and $G^{\alpha\beta\gamma\delta}$ are constants, $c^{\alpha\beta}$ are possibly divergent $c$-numbers and the $q$-number Schwinger terms are antisymmetric in $\alpha\beta$.

We give now the consequences of eqs. (109-111) for asymptotic sum rules at infinite momentum in electroproduction and neutrino-production [56] [57].

For electroproduction one defines [57]

$$-F_l(\omega) = \lim \frac{1}{M}\left[\frac{\nu}{q^2} W_2(q^2, \nu) + M^2 W_1(q^2, \nu)\right] \tag{112}$$

$$F_t(\omega) = \lim MW_1(q^2, \nu) \tag{113}$$

where $q^2$ is the squared virtual photon momentum, $\nu = qP$, $P$ being the target nucleon momentum, $M^2 = P^2$, $\omega = -q^2/\nu$, $W_1$ and $W_2$ are the structure functions for inelastic electron scattering and the limit is for $q^2 \to \infty$ and $\omega$ fixed. The Callan-Gross sum rules are [56] [57]:

$$\int_0^2 d\omega\omega F_{l(t)}(\omega) = (\pm) \lim_{P_z\to\infty} \frac{i}{2} \int \frac{d^3x}{P_0} \langle P_z | [\partial_0 j_{l(t)}^{em}(\vec{x}, 0), j_{l(t)}^{em}(0)] | P_z \rangle \tag{114}$$

where $j_l^{em}$ is the component along $z$ and $j_t^{em}$ is a transverse component of the e. m. current; the sign minus applies to. From eq. (111) one finds:

$$I_t \equiv \int_0^2 d\omega\omega F_t(\omega) = \frac{4}{3}\frac{c_1}{2} \tag{115}$$

$$I_l = \int_0^2 d\omega\omega F_l(\omega) = -\frac{4}{3}\frac{c_1 + c_2}{2}. \tag{116}$$

It can also be shown that there in no $q$-number Schwinger term in the equal-time-commutator $[j_0, j_i]$. Under a certain convergence con-

dition (into which we shall not enter here) this requires $F_\varrho(\omega) = 0$ and thus, by eq. (116), the relation $c_1 = -c_2$.

For high energy neutrinoproduction one has [57]

$$\sigma_{\text{tot}}^{\bar{\nu}p(n)} + \sigma_{\text{tot}}^{\nu p(n)} \to \frac{G^2 ME}{4\pi} a_{p(n)} \tag{117}$$

$$a_{p(n)} = \lim_{P_z \to \infty} (-1) \int \frac{d^3x}{P_0} \Big\langle P_z \Big| \frac{4}{3} [\partial_0 j_x(\vec{x}, 0), j_x^*(0)] - - [\partial_0 j_x(\vec{x}, 0), j_x^+(0)] \pm \frac{2}{3} [\partial_0 j_x(\vec{x}, 0), j_y^*(0)] \Big| P_z \Big\rangle \tag{118}$$

where $\sigma_{\text{tot}}^{\nu p}$, $\sigma_{\text{tot}}^{\nu n}$ are the total neutrino cross-sections on proton or neutron target respectively, $E$ is the incident laboratory neutrino energy, and in eq. (118) the sign minus in front of the last commutator applies to $n$; $j_\mu$ is the Cabibbo current. From eqs. (109) and (111) one finds:

$$a = a_p = a_n = 2(4I_t + 3I_l). \tag{119}$$

Both the linear rise in eq. (117) and the relations in eq. (119) are consistent with data [58] [59]. Assuming $c_1 = -c_2$ (see before) one has $a = 8I_t$. From SLAC data one obtains $a = 2.8 \pm 0.4$. Neglecting $\Delta S = 1$ transitions, one can then predict

$$\sigma^{\nu p} + \sigma^{\nu n} \cong \frac{G^2 ME}{\pi} (0.7 \pm 0.1)$$

to be compared with recent data (the last reference in [58]) which suggest

$$\sigma^{\nu p} + \sigma^{\nu n} \cong \frac{G^2 ME}{\pi} (1 \pm 0.3) .$$

In addition one obtains, in the same limits:

$$\frac{a^{\nu p}(\Delta S = 1) + a^{\bar{\nu}p}(\Delta S = 1)}{a^{\nu p}(\Delta S = 0) + a^{\bar{\nu}p}(\Delta S = 0)} = \text{tg}^2\,\theta \tag{120}$$

where $a^{\nu p}(\Delta S = 1)$, $a^{\nu p}(\Delta S = 0)$ are the coefficients which occur in the expressions for the cross-sections into $S = 1$ ($S = 0$) states according to eq. (117), and $\theta$ is the Cabibbo angle. One also obtains from eqs. (109) and (111) sum rules analogous to those in eqs. (115) and (116) for the functions $\tilde{F}_1(\omega)$, $\tilde{F}_2(\omega)$ and $\tilde{F}_3(\omega)$, defined by Bjorken [57], which are the « deep-inelastic » limits of the structure functions for neutrinoproduction.

In particular:

$$\int_0^2 d\omega\omega\tilde{F}^3(\omega) = 0 \,. \tag{121}$$

We now turn to the problem of electromagnetic mas differences. Their logarithmic divergences, isolated according to Bjorken's technique depend on the coefficients $G^{\alpha\beta\gamma\delta}$ in eq. (111). In principle such coefficients are non-zero and the presence of terms transforming like $(3,\bar{3}) \oplus (\bar{3},3)$ in commutators of current components may even be welcomed in relation to some difficulties with second order electromagnetic corrections. We simply note that one can possibly avoid the appearance of such terms if one is willing to postulate that the Jacobi-identity holds for the triple product $[Q^\alpha(0), [j_i^\beta(\vec{x}, 0), \partial_0 j_k^\gamma(0) - \partial_k j_i^\gamma(0)]]$. In such a case electromagnetic mass differences would be free of logarithmic divergences and thus finite even if not necessarily calculable from low energy parameters. The assumption is however rather strong. For a detailed investigation we refer to ref. (60).

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# The ω-ρ Electromagnetic Mixing.

I wish to present a work made in collaboration with F. M. Renard and L. Stodolsky [1] about the mixing of $\varrho$ and $\omega$ mesons due to electromagnetic interactions. The recent Orsay experiment [2] on electron-positron annihilation into two $\pi$ mesons was the motivation of our interest. This talk closely follows the letter referred to as [1] and details about formalism can also be found in the Boulder Lecture notes of the author [3].

## I. Experimental evidences.

1. – Let us begin with the Orsay experiment on

$$e^+ + e^- \Rightarrow \pi^+ + \pi^-$$

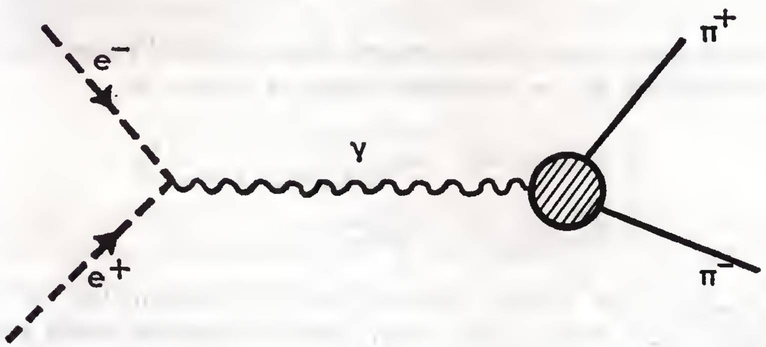


Fig. 1.

where six points in the energy range of the $\omega$ meson have been measured for the total cross section [2] in addition to the seven points already obtained outside that region [4].

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In the one-photon exchange approximation represented on fig. 1 the general structure of the total cross section for $e^+ e^-$ annihilation into $2\pi$ is given by

$$\sigma_{\text{tot}}(e^+e^- \Rightarrow \pi^+\pi^-) = \frac{\pi\alpha^2}{3}\frac{1}{s}\left(1 - \frac{4m_\pi^2}{s}\right)^{3/2} |F_\pi(s)|^2 \tag{1}$$

where $\alpha$ is the fine structure constant, $\alpha = 1/137$, and $s$ the square of the total energy in the centre-of-mass system. The $\pi$-meson electromagnetic form factor is normalized to unity at $s = 0$

$$F_\pi(0) = 1 .$$

2. – In the region of experiments

$$500 \text{ MeV} \leq \sqrt{s} \leq 900 \text{ MeV}$$

the $\pi$-meson electromagnetic form factor can be described by an isobaric model taking into account only two contributions

*a*) the dominating amplitude due to the $\varrho$ meson;

*b*) the electromagnetic amplitude due to the $\omega$ meson.

$$F_\pi(s) = \frac{m_\varrho^2}{W_\varrho(s) - s} C_\varrho + \frac{m_\omega^2}{W_\omega(s) - s} C_\omega . \tag{2}$$

The diagonal terms of the squared mass matrix $W(s)$ can be reasonably represented in the considered range of energy by

$$\left\| \begin{aligned} & W_\varrho(s) \simeq m_\varrho^2 - im_\varrho \left[\frac{K_{\pi\pi}(s)}{K_{\pi\pi}(m_\varrho^2)}\right]^3 \frac{m_\varrho}{\sqrt{s}} \Gamma_\varrho \\ & W_\omega(s) \simeq m_\omega^2 - im_\omega \Gamma_\omega \end{aligned} \right. \tag{3}$$

where $K_{\pi\pi}(s)$ is the $\pi$-meson centre-of-mass momentum. Let us remark that such a weak form of the vector meson dominance model certainly works because of the existence of $\varrho$ and $\omega$ mesons as physically realizable unstable intermediate states.

3. – Each contribution in equation (2) is described by four real parameters: the mass $m_a$, the width $\Gamma_a$, the complex coupling constant $C_a$.

The Orsay data have been analyzed in the following way. The $\varrho$-meson contribution has been represented by a form suggested by Frazer and

Fulco [5] in 1959 and by Gounaris and Sakurai [6] in 1968, starting from an effective range formula for the $\pi$-$\pi$ phase shift in the state $J = 1$, $I = 1$. The equivalent formulation, here, is simply to correct the universality of the $\varrho$ coupling by a width-dependent factor

$$C_\varrho \simeq 1 + d\,\frac{\Gamma_\varrho}{m_\varrho}$$

where $d$ is computed from the actual $\varrho$ mass to be $d \simeq 0.48$. For the $\omega$-meson contribution, the mass and the width have been taken to their world average values [7]

$$m_\omega = 783 \text{ MeV} \qquad \Gamma_\omega = 12.3 \text{ MeV}$$

and we have the complex parameter $C_\omega$ free, which one can represent as

$$C_\omega = \frac{f_{\omega 2\pi}}{f_\omega}$$

where $f_{\omega 2\pi}$ is the decay coupling constant for the process $\omega \Rightarrow \pi^+\pi^-$

$$\Gamma(\omega \Rightarrow \pi^+\pi^-) = \frac{2}{3}\,\frac{|f_{\omega 2\pi}|^2}{4\pi}\,\frac{K^3_{\pi\pi}(m^2_\omega)}{m^2_\omega}$$

and $f_\omega^{-1}$ is the photon-$\omega$-meson coupling constant describing the radiative decay $\omega \Rightarrow e^+e^-$ in the one-photon exhange model

$$\Gamma(\omega \Rightarrow e^+e^-) = \frac{4\pi\alpha^2}{3}\,\frac{m_\omega}{|f_\omega|^2}\,.$$

The knowledge of $|C_\omega|$ combined with the value of $|f_\omega|$ as deduced from a previous measurement [8] of the process $e^+e^- \Rightarrow \pi^+\pi^-\pi^0$ will allow us to compute the electromagnetic decay width $\Gamma(\omega \Rightarrow \pi^+\pi^-)$. The phase of $C_\omega$ with respect to $C_\varrho$ can also be measured and is called $\Phi_{2\pi}$.

4. – The results of the Orsay experiment are the following [2]

$$m_\varrho = (773.5 \pm 5.4) \text{ MeV} \qquad \Gamma_\varrho = (110.7 \pm 5.3 \text{ MeV})$$

$$\Gamma^{\frac{1}{2}}(\omega \Rightarrow \pi^+\pi^-) = (0.63 \pm 0.23) \text{ MeV}^{\frac{1}{2}}$$

$$\Phi_{2\pi} = (196 \pm 28)^\circ\,.$$

5. – The $\omega$-$\varrho$ electromagnetic interference has also been seen in other processes where the vector mesons are produced by a strong interaction mechanism. Let us quote some experiments:

*a*) By Flatté et al. [9] in the reaction $K^- p \Rightarrow \Lambda\pi^+\pi^-$ assuming coherence in the production, the result is

$$\Gamma^{\frac{1}{2}}(\omega \Rightarrow \pi^+\pi^-) = (0.51 \pm 0.09)\ \text{MeV}^{\frac{1}{2}} .$$

*b*) By Goldhaber et al. [10] in the reaction $\pi^+ p \Rightarrow \pi^+\pi^-\pi^+ p$ with the result assuming again coherence in the production

$$\Gamma^{\frac{1}{2}}(\omega \Rightarrow \pi^+\pi^-) \simeq (0.57 \pm 0.27)\ \text{MeV}^{\frac{1}{2}} .$$

*c*) A similar effect has also been observed at CERN [11].

## II. Mixing formalism.

1. – Since we are interested in problems like

$$e^+ + e^- \Rightarrow \pi^+ + \pi^-$$

measured as a function of the energy $\sqrt{s}$ across broad resonances, instead of using the Weisskopf-Wigner [12] time-dependent method we prefer to work in a formalism giving the transition amplitude.

More precisely, we use the propagator method introduced by Jacob and Sachs [13] and we are interested in the properties of the generalized squared mass matrix $W$.

2. – The coefficient of $g_{\mu\nu}$ in the vector meson propagator is written as

$$F(s) = \frac{1}{W(s) - sI} .$$

$I$ is the projection operator on the $\omega$-$\varrho$ space, e. g. the unit operator in that space and $W(s)$ is a $2 \times 2$ matrix. Let us call the pure eigenstates of $I$ isospin $\varrho_0$ and $\omega_0$

$$< \varrho_0 | \varrho_0 > = 1 = < \omega_0 | \omega_0 > \qquad < \omega_0 | \varrho_0 > = < \varrho_0 | \omega_0 > = 0 .$$

In the absence of e. m. interactions, $W(s)$ has a diagonal representation in such a basis.

In the presence of e. m. interactions, there are electromagnetic corrections to $W$, especially the appearance of non-diagonal elements $W_{\varrho_0\omega_0}$ and $W_{\omega_0\varrho_0}$.

3. – The physical $\varrho$ and $\omega$ particles are simply associated with complex poles of the propagator in the second sheet or equivalently in a time-dependent formalism are those states having a well-defined life time. To satisfy these requirements, let us diagonalize, for each value of $s$, the matrix $W(s)$, performing a linear transformation $C(s)$ in the two-dimensional $\varrho$-$\omega$ space.

In the lowest order with respect to electromagnetic interactions, we simply write the right eigenvectors of $W(s)$ as

$$(4)\qquad \left\| \begin{aligned} &|\varrho(s)> = |\varrho_0> - \varepsilon_1(s)\,|\omega_0> \\ &|\omega(s)> = |\omega_0> + \varepsilon_2(s)\,|\varrho_0> \end{aligned} \right.$$

where $\varepsilon_1(s)$ and $\varepsilon_2(s)$ are two complex mixing parameters related to the matrix elements of $W(s)$ in the original basis by

$$(5)\qquad \left\| \varepsilon_1(s) = -\frac{W_{\omega_0\varrho_0}(s)}{W_{\varrho_0\varrho_0}(s) - W_{\omega_0\omega_0}(s)} \qquad \varepsilon_2(s) = -\frac{W_{\varrho_0\omega_0}(s)}{W_{\varrho_0\varrho_0}(s) - W_{\omega_0\omega_0}(s)}\,. \right.$$

Since $W(s)$ is not hermitian, the eigenvectors $|\varrho>$ and $|\omega>$ are not necessarily orthogonal

$$(6)\qquad <\omega(s)\,|\,\varrho(s)> = \bar{\varepsilon}_2(s) - \varepsilon_1(s) \neq 0\,.$$

In other terms, the linear transformation $C(s)$ which diagonalizes $W$ is not in general unitary so that the left eigenvectors of $W$ are not $<\varrho|$ and $<\omega|$ but

$$(7)\qquad \left\| \begin{aligned} &<\tilde{\varrho}(s)| = <\varrho_0| - \varepsilon_2(s) <\omega_0| \\ &<\tilde{\omega}(s)| = <\omega_0| + \varepsilon_1(s) <\varrho_0|\,. \end{aligned} \right.$$

Let us summarize two crucial properties of these bases

*a*) orthogonality of the two bases

$$<\tilde{\varrho}|\varrho> = <\tilde{\omega}|\omega> = 1$$

$$<\tilde{\varrho}|\omega> = <\tilde{\omega}|\varrho> = 0$$

*b*) decomposition of the identity $I$

$$I = |\varrho><\tilde{\varrho}| + |\omega><\tilde{\omega}|\,.$$

4. – Consider now a process $1 \Rightarrow 2$ dominated by the vector meson contributions in the $s$ channel. The resonating part of the transition operator $T$ is proportional to [14] [3]

$$T \alpha \frac{|\varrho > < \tilde{\varrho}|}{W_\varrho(s) - s} + \frac{|\omega > < \tilde{\omega}|}{W_\omega(s) - s} \tag{8}$$

where $W_\varrho$ and $W_\omega$ are the eigenvalues of $W$ associated to the physical particles $\varrho$ and $\omega$. Explicit forms of $W_\varrho$ and $W_\omega$ have been previously given in equation (3) for a limited range of values of the energy.

For the important case of electron-positron annihilation into a final state $F$ where $F$ can be $\pi^+\pi^-$, $\pi^+\pi^-\pi^0$, $\pi^0\gamma$, etc. the total cross section in the resonance region is written

$$\sigma_{\text{tot}}(e^+ + e^- \Rightarrow F) = \frac{(4\pi\alpha)^2}{s} \gamma_F(s) \left| \sum_a \frac{f_{aF}}{f_{\tilde{a}}} \frac{m_a^2}{W_a(s) - s} \right|^2 \tag{9}$$

where $\gamma_F(s)$ is a known kinematical factor associated to the final state $F$. The $f_{aF}$ 's are decay coupling constants and the partial decay width $\Gamma(a \Rightarrow F)$ is simply given by

$$\Gamma(a \Rightarrow F) = m_a^{-1} \, |f_{aF}|^2 \, \gamma_F(m_a^2) \, . \tag{10}$$

The coupling constants $f_{\tilde{a}}^{-1}$ describe the vector meson excitation by a $e^+e^-$ pair in the one-photon exchange model.

5. – The constraints on the vector-meson propagator due to the unitarity property of the $S$ matrix can be derived in a straightforward way from equation (8). Because of the lack of time we only give the results [3]

$\alpha$) We define the set of functions

$$\sigma_{ba}(s) = \underset{F}{S} < F \,|\, T \,|\, b >^* < F \,|\, T \,|\, a > \tag{11}$$

which correspond to the total widths by

$$\Gamma_a = m_a^{-1} \sigma_{aa}(m_a^2) \, . \tag{12}$$

Here $a$, $b$ can be either the physical states $\varrho$, $\omega$ or the isospin eigenstates $\varrho_0$, $\omega_0$.

$\beta$) For the diagonal elements $a = b$, the unitarity constraints are simply

$$-\operatorname{Im} W_\varrho(s) = \sigma_{\varrho\varrho}(s) \qquad -\operatorname{Im} W_\omega(s) = \sigma_{\omega\omega}(s) \, . \tag{13}$$

$\gamma$) For the non-diagonal elements we obtain a Bell-Steinberger type relation measuring the nonorthogonality of the physical states $\varrho$ and $\omega$.

(14) $$\frac{1}{2i}\left[\overline{W}_\omega(s) - \dot{W}_\varrho(s)\right] < \omega(s)\,|\,\varrho(s) > = \sigma_{\omega\varrho}(s)\,.$$

$\delta$) In the orthogonal basis $\varrho_0\omega_0$, the constraints look formally simpler. If we split the matrix $W$ into its hermitian and skew hermitian parts

(15) $$W = R - i\Sigma$$

the unitarity relations are simply $\Sigma = \sigma$, both matrices being written in the $\varrho_0\omega_0$ basis.

6. – If time-reversal invariance holds, the matrix $W(s)$ is symmetric

(16) $$W_{\varrho_0\omega_0}(s) = W_{\omega_0\varrho_0}(s)$$

therefore the two mixing parameters are equal

(17) $$\varepsilon_1(s) = \varepsilon_2(s)$$

and all the matrix elements of $R$ and $\sigma$ in the $\varrho_0\omega_0$ basis become *real* func tions of $s$.

## III. General features of the ω-ρ mixing.

1. – The natural order of magnitude expected for an electromagnetic amplitude $\omega \Rightarrow \pi^+\pi^-$ as compared with the amplitude $\varrho \Rightarrow \pi^+\pi^-$ is obviously the fine structure constant $\alpha$.

For instance, in the one-photon exchange model

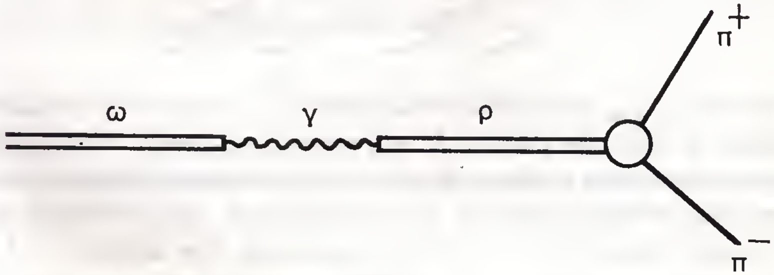


Fig. 2.

a straightforward calculation gives

$$\left|\frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}}\right| \simeq 1.3\alpha\,.$$

The Orsay measurement, expressed in the same unit is

$$\left|\frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}}\right|_{\exp} \simeq (8.2 \pm 2.7)\alpha\,.$$

Clearly, the one-photon exchange model cannot explain the experimental data and we must look more carefully at that problem.

It seems that the dominant effect is in fact located in the mixing parameters $\varepsilon_1$ and $\varepsilon_2$ wich can be of an order of magnitude larger of $\alpha$ because of the quasi degeneracy in mass of $\varrho$ and $\omega$.

However the $\omega \Rightarrow 2\pi$ decay in this formalism can come either from the direct transition $\omega_0 \Rightarrow 2\pi$ or from the strong decay $\varrho_0 \Rightarrow 2\pi$, the $\varrho_0$ being mixed into the physical $\omega$ by $\varepsilon_2$. From equations (4)

$$\frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}} = \frac{f_{\omega_0 2\pi}}{f_{\varrho 2\pi}} + \varepsilon_2\,. \tag{18}$$

Nevertheless with a mixing parameter $\varepsilon_2$ larger than $\alpha$, the direct electromagnetic transitions like $\omega_0 \Rightarrow 2\pi$ or $\varrho_0 \Rightarrow 3\pi$ should still be of order $\alpha$ as compared respectively with $\varrho_0 \Rightarrow 2\pi$ or $\omega_0 \Rightarrow 3\pi$.

2. – Let us go back to formula (5) giving $\varepsilon_2$ in terms of the matrix elements of $W$

$$\varepsilon_2 = -\frac{W_{\varrho_0\omega_0}}{W_{\varrho_0\varrho_0} - W_{\omega_0\omega_0}}\,.$$

Using the decomposition (15), $\varepsilon_2$ is written as the sum of two terms

$$\varepsilon_2 = -\frac{R_{\varrho_0\omega_0}}{W_{\varrho_0\varrho_0} - W_{\omega_0\omega_0}} + i\,\frac{\sigma_{\varrho_0\omega_0}}{W_{\varrho_0\varrho_0} - W_{\omega_0\omega_0}}\,. \tag{19}$$

The term $R_{\varrho_0\omega_0}$ comes from transitions to a virtual intermediate state containing at least one photon. It is a typical self-energy term of electromagnetic nature such as those responsible for the mass differences between charged and neutral mesons in the same isotopic spin multiplet. It can be estimated using $SU(3)$ or $SU(6)$ arguments. For instance a $U$ spin invariance of electromagnetic interactions combined with a medium strong

interaction mixing of the singulet and the octuplet representations with an angle $\theta$ gives [16]

$$\frac{\sqrt{3}}{2}\{\cos\theta(R_{\varrho_0\varphi_0}+R_{\varphi_0\varrho_0})+\sin\theta(R_{\varrho_0\omega_0}+R_{\omega_0\varrho_0})\}=(m^2_{\varrho_0}-m^2_{\varrho^+})+(m^2_{K^{*+}}-m^2_{K^{*0}}).$$

Further considerations allow, as an order of magnitude [16]

$$\frac{1}{m_\varrho}\left|\operatorname{Re} R_{\varrho_0\omega_0}\right|\simeq(5-10)\ \text{MeV}\,.$$

The term $\sigma_{\varrho_0\omega_0}$ comes from the existence of real intermediate states like $2\pi$, $3\pi$, $\pi^0\gamma$, etc. and it can be represented as the sum of its various contributions as shown on fig. 3.

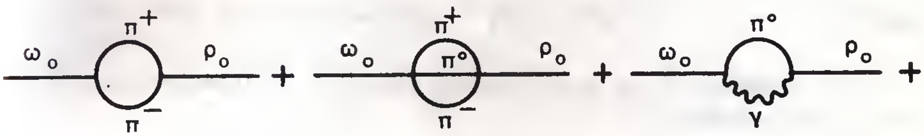


Fig. 3.

Accepting the previous order of $\alpha$ argumentation and using the Schwartz inequality we obtain

$$\frac{1}{m_\varrho}|\sigma^{(2\pi)}_{\varrho_0\omega_0}|\leq\Gamma^{\frac{1}{2}}(\varrho_0\Rightarrow 2\pi)\Gamma^{\frac{1}{2}}(\omega_0\Rightarrow 2\pi)\simeq\alpha\Gamma(\varrho_0\Rightarrow 2\pi)\simeq 0.8\ \text{MeV}$$

$$\frac{1}{m_\varrho}|\sigma^{(3\pi)}_{\varrho_0\omega_0}|\leq\Gamma^{\frac{1}{2}}(\varrho_0\Rightarrow 3\pi)\Gamma^{\frac{1}{2}}(\omega_0\Rightarrow 3\pi)\simeq\alpha\Gamma(\omega_0\Rightarrow 3\pi)\simeq 0.07\ \text{MeV}$$

$$\frac{1}{m_\varrho}|\sigma^{(\pi^0\gamma)}_{\varrho_0\omega_0}|\leq\Gamma^{\frac{1}{2}}(\varrho_0\Rightarrow \pi^0\gamma)\Gamma^{\frac{1}{2}}(\omega_0\Rightarrow \pi^0\gamma)<0.7\ \text{MeV}\ [17]$$

The other states are suppressed by phase-space considerations and a rough limit for $\sigma_{\varrho_0\omega_0}$ seems to be

$$\frac{1}{m_\varrho}|\sigma_{\varrho_0\omega_0}|\lesssim 1.6\ \text{MeV}\,.$$

3. – According to equation (19) the parameter $\varepsilon_2$ can be split into two terms

$$\varepsilon_2=\varepsilon_2^R+\varepsilon_2^\sigma$$

and from the above estimates we have

$$|\varepsilon_2^R| \simeq (6.5 - 13)\alpha$$

$$|\varepsilon_2^\sigma| \lesssim 2\alpha\,.$$

4. – In an analogous way the parameter $\varepsilon_1$ is written as

$$\varepsilon_1 = \varepsilon_1^R + \varepsilon_1^\sigma\,.$$

The matrices $R$ and $\sigma$ being hermitian

$$R_{\omega_0\varrho_0} = \overline{R}_{\varrho_0\omega_0} \qquad \sigma_{\omega_0\varrho_0} = \bar{\sigma}_{\varrho_0\omega_0}$$

we have

$$(20) \qquad |\varepsilon_1^R| = |\varepsilon_2^R| \qquad |\varepsilon_1^\sigma| = |\varepsilon_2^\sigma|\,.$$

The equality of the corresponding phases is a consequence of time-reversal invariance.

## IV. The $\omega \Rightarrow 2\pi$ decay.

1. – The direct transition $\omega_0 \Rightarrow 2\pi$ affects the decay $\omega \Rightarrow 2\pi$ in two ways:

*a*) through the first term $f_{\omega_0 2\pi}$ in equation (18);

*b*) through the $2\pi$ contribution to the part $\varepsilon_2^\sigma$ of $\varepsilon_2$.

As a remarkable fact one trivially checks by direct calculation, these two contributions partially cancel. The resulting importance of $f_{\omega_0 2\pi}$ in equation (18) comes out with a damping factor of order $\Gamma_\omega/\Gamma_\varrho$ and this because the $2\pi$ channel dominates this problem.

Therefore $f_{\omega_0 2\pi}$ has only a small effect on $f_{\omega 2\pi}$ and even an unusually large direct transition $\omega_0 \Rightarrow 2\pi$ cannot be responsible for the observed $\omega \Rightarrow 2\pi$ decay.

2. – We then introduce a parameter $\varepsilon_2'^\sigma$ defined as $\varepsilon_2^\sigma$ but without the contribution coming from the real $2\pi$ state

$$(21) \qquad \frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}} = \varepsilon_2^R + \varepsilon_2'^\sigma + o\left(\frac{\Gamma_\omega}{\Gamma_\varrho}\,\frac{f_{\omega_0 2\pi}}{f_{\varrho 2\pi}}\right).$$

In any case, what can explain the size of $f_{\omega 2\pi}/f_{\varrho 2\pi}$?

The estimate of $|\varepsilon_2'^{\sigma}|$ is reduced by a factor 2 as compared to that of $|\varepsilon_2^{\sigma}|$ and there seems to be no choice but to make the self-energy terms contained in $\varepsilon_2^R$. So that

$$\frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}} \simeq \varepsilon_2^R = -\frac{R_{\varrho_0\omega_0}}{W_{\varrho_0\varrho_0} - W_{\omega_0\omega_0}} . \tag{22}$$

From the Orsay measurement of $\Gamma^{\frac{1}{2}}(\omega \Rightarrow 2\pi)$ we obtain

$$|\varepsilon_2^R| \simeq 0.06 \pm 0.02 .$$

The corresponding self energy of 6 MeV fits very well the models [16].

3. – Let us call the phases of $\varepsilon_1^R$ and $\varepsilon_2^R$, $\varphi_1$ and $\varphi_2$. If time-reversal invariance holds, the function $R_{\varrho_0\omega_0}$ is real, the phases $\varphi_1$ and $\varphi_2$ and a prediction can be made for their common value $\varphi$

$$\varphi = (-79 \pm 6)^\circ \qquad \text{or} \qquad \varphi = (+101 \pm 6)^\circ .$$

The error is essentially due to the uncertainty on the $\varrho$-meson mass taken as $m_\varrho = (772 \pm 6)$ MeV.

On the other hand the variation with the energy of the phase in the range $m_\varrho \leq \sqrt{s} \leq m_\omega$ is less than 1°.

4. – Let us go back to the phase $\Phi_{2\pi}$ as measured in the Orsay experiment, assuming again time-reversal invariance. The photon vector meson coupling constants $f_a^{-1}$ have a small phase $\varphi_a$ because of the mixing

$$\Phi_{2\pi} = \varphi_2 + \varphi_\omega - \varphi_\varrho . \tag{23}$$

Using the previous result for $|\varepsilon|$ we finally obtain

$$\begin{array}{lll} \varphi_\omega - \varphi_\varrho \simeq -10^\circ & \Phi_{2\pi} \simeq -89^\circ & \text{if } \varphi = -79^\circ \\ \varphi_\omega - \varphi_\varrho = +11^\circ & \Phi_{2\pi} = +112^\circ & \text{if } \varphi = +101^\circ . \end{array}$$

Both predictions are in disagreement with the Orsay measurement [1]

$$\Phi_{2\pi} = (-164 \pm 28)^\circ .$$

More statistics are obviously needed to obtain a reliable determination of $\Phi_{2\pi}$ but if this experimental result is confirmed, our theory of the elec-

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[1] In the presentation of data Orsay people use an opposite phase to ours and the data to compare with theory is $\Phi_{2\pi} = (+164 \pm 28)^\circ$.

tromagnetic $\omega$-$\varrho$ mixing based on purely phenomenological grounds fails and we have to reconsider other ways to reconcile theory and experiment as for instance

*a*) violation of time reversal in electromagnetic interactions;
*b*) a violation of isotopic spin in strong interactions.

## V. The $\rho \Rightarrow 3\pi$ decay.

1. – It will be very interesting to detect the $\omega$-$\varrho$ interference in the $3\pi$ final state. Crudely speaking the roles of the $\omega$ and $\varrho$ mesons being exchanged, the magnitude of the interference effect into $e^+e^- \Rightarrow 2\pi$ and $e^+e^- \Rightarrow 3\pi$ are related by a factor of the order

$$\left(\frac{f_{\omega_0}}{f_{\varrho_0}}\right)^2 \left(\frac{\Gamma_\omega}{\Gamma_\varrho}\right)^2 \simeq 0.11\,.$$

Therefore the measurement of the $\omega$-$\varrho$ interference in the $3\pi$ mode will be an order of magnitude more difficult than in the $2\pi$ mode assuming comparable statistics.

2. – If the order of $\alpha$ argument is correct for the $\varrho_0 \Rightarrow 3\pi$ transition the dominant part of the $\varrho \Rightarrow 3\pi$ decay is also due to the self-energy terms contained in $\varepsilon_1^R$ so that

$$\frac{f_{\varrho 3\pi}}{f_{\omega 3\pi}} \simeq -\varepsilon_1^R = \frac{W_{\omega_0\varrho_0}}{W_{\varrho_0\varrho_0} - W_{\omega_0\omega_0}}\,. \tag{24}$$

The first consequence is the relation between partial widths

$$\frac{\Gamma(\varrho \Rightarrow 3\pi)}{\Gamma(\omega \Rightarrow 3\pi)} = \frac{\Gamma(\omega \Rightarrow 2\pi)}{\Gamma(\varrho \Rightarrow 2\pi)}\,. \tag{25}$$

On the other hand, $W_{\varrho_0\omega_0}$ and $W_{\omega_0\varrho_0}$ being complex conjugate functions, the phases $\varphi_1$ and $\varphi_2$ of $\varepsilon_1^R$ and $\varepsilon_2^R$ are related by

$$\varphi_1 + \varphi_2 = 2\varphi = (202 \pm 12)^\circ\,. \tag{26}$$

The phase $\Phi_{3\pi}$ experimentally measured in a $e^+e^- \Rightarrow \pi^+\pi^-\pi^0$ experiment is given from equation (24) by

$$\Phi_{3\pi} = \varphi_1 - \varphi_\omega + \varphi_\varrho - 180^\circ\,. \tag{27}$$

Combining equations (23), (26) and (27) we obtain a second relation

$$\Phi_{2\pi} + \Phi_{3\pi} = (22 \pm 12)^{\circ} . \tag{28}$$

Both predictions (25) and (28) are independent of time-reversal invariance.

3. – Assuming now time-reversal invariance and the coupling constant $f_{\omega 2\pi}$ and $f_{\varrho 3\pi}$ measured in magnitude and phase, we can test the idea of the present formalism by eliminating the mixing parameter $\varepsilon$ between these two amplitudes

$$\frac{f_{\omega 2\pi}}{f_{\varrho 2\pi}} + \frac{f_{\varrho 3\pi}}{f_{\omega 3\pi}} = \frac{f_{\omega_0 2\pi}}{f_{\varrho_0 2\pi}} + \frac{f_{\varrho_0 3\pi}}{f_{\omega_0 3\pi}} . \tag{29}$$

The right-hand side of this equality should be of the order $\alpha$ that is much smaller than each term of the left-hand side.

## VI. Concluding remarks.

Analogous analyses can be made for all the decay modes of vector mesons like $\pi^0\gamma$ [1] [3], $\eta\gamma$, $e\bar{e}$ [1], [3] etc.

For the future indeed the $\omega$-$\varrho$ electromagnetic mixing phenomena can be used to determine the relative phase of the $\omega$ and $\varrho$ production amplitudes. Experimentally, a global relative phase can only be measured as here $\Phi_{2\pi}$ or $\Phi_{3\pi}$. If the relative phases for the decay are experimentally known and theoretically understood — for instance if the phase $\varphi$ turns out to be $-79^{\circ}$ as predicted above — then we will be able to extract the phases of the production amplitudes and therefore to learn very useful information about the production mechanism of $\varrho$ and $\omega$ mesons. Such a remark applies to the type of experiments performed in references [9], [10] and [11].

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[17] From reference [7] we use.

$$\Gamma(\omega \Rightarrow \pi^0\gamma) \simeq 1.2 \text{ MeV} \qquad \Gamma(\varrho \Rightarrow \pi\gamma^0) < 0.4 \text{ MeV}.$$

G. C. WICK (*)

# Closing Address.

In the original program of this meeting, Professor Gell-Mann was expected to deliver the Closing Address; owing to an unavoidable change in his travel schedule, I was asked to replace him in this role on rather short notice. I must hope for some good will on your side, in case my effort shows too clearly the effect of improvisation.

I take it to be my task, to summarize what we have learned in the course of these few days, and to tell you, according to my best judgment, which were the highlights of the meeting and what was the general sense of the discussions we have heard. Also, because the meeting was split in half between Torino and Rome, and many, who are now here, did not attend the first half of the meeting, it may be appropriate for me to acquaint them, as the occasion arises, whit some of the things that went on there. With regard to the last two days of the meeting, I shall content myself with a few general remarks.

Let me, however, express first of all our feelings of gratitude to the two eminent Academies and to all those who have contributed with their time to the success of this meeting, in particular to the distinguished Russian colleagues, who have come a long way to help us honour their great compatriot. Without them, this meeting would have been incomplete.

Now, to get started with my task, let me recall the very appropriate distinction made here yesterday by Professor Gell-Mann concerning the kinds of theoretical schemes, that one can try to set up in order to describe and analyse a certain body of experimental data. As he pointed out, while the notion of a " complete dynamical interpretation " of the observations (the " Newtonian " ideal of a theory) exerts, for obvious reasons, a strong appeal on all of us, it does not follow, that it is the most fruitful model to follow at all times. There are cases, when the development of the subject is still so remote from the Newtonian stage, that an entirely different kind of theoretical effort may be far more fruitful. Gell-Mann,

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in fact, expressed a strong suspicion, that this may be the case in the field of High Energy and Elementary Particle Physics, and he suggested that the great event we are commemorating here, the discovery, by Mendeleev, of the Periodic System of the chemical elements, may offer us a model of theoretical effort, which we might wisely try to imitate. It is hardly necessary to say, that even such a broad, qualitative, semi-empirical scheme as Mendeleev's System already presupposes the previous accumulation of an enormous mass of experimental findings. In fact, one can say that Mendeleev's discovery was the crowning achievement of at least a century of painstaking investigations, an achievement which was made possible only by his superb command of an enormous mass of detailed facts. This came out very vividly from the opening speeches by the Chemists in Torino, especially from the remarks made by Professor Spitzin at the beginning of his talk on " Hundred Years of the Periodic Law ". I mentioned before the century preceding Mendeleev, but, of course, the hundred years of the title are those following the discovery, and Professor Spitzin's talk was a demonstration of the amazing predictive value of the scheme during this long period of time.

It is clear that the discovery of the semi-empirical scheme of the Periodic System was a very essential step on the way to a full inderstanding of the inner dynamical structure of atoms and molecules. What came next, we heard in a fascinating and entertaining speech by Professor Weisskopf. The hero of this part of the story is, of course, Niels Bohr. Again, as in the case of Mendeleev, it was Bohr's command of an extraordinary array of apparently unrelated facts from chemistry, spectroscopy, X-ray spectroscopy, magnetism and so on, and his uncanny intuition in perceiving relations between them, that led to the great synthesis of the early twenties, in which Bohr attained a deep understanding of the inner structure of atoms as the source of the periodicities discovered by Mendeleev. Still, even after such an enormous progress, one can hardly say that the theory of atoms had achieved the Newtonian ideal. In this connection, Professor Weisskopf did an interesting bit of historical research, and discovered some very amusing and instructive comments by Pauli, for which I must, however, refer you to his address. The Newtonian stage in atomic theory was attained, as most people will agree, with quantum mechanics. It is here that we find at last an exact mathematical formulation of a few principles, from which one can derive, by exact or reasonably accurate calculations, an enormous mass of quantitative predictions, just as in celestial mechanics.

Now, returning to Gell-Mann's discussion, it seems quite possible that the world of elementary particles is just as rich and complicated as that of atoms, and if that is the case, it is natural to ask ourselves

whether it is realistic to be as ambitiously " Newtonian " as we often claim to be. Perhaps we do not even have enough facts in our possession to imitate Mendeleev, and set up a scheme that manages to include in a relatively short statement, like the Periodic Law, a large number of disconnected facts and observed regularities. Such a scheme, if true, would have predictive value, and would in any case be a very important step forward in our search for the true exact laws behind it all. Whether such a synthesis is possible at present, we can only find out by trying. Just as in fact, to temper something I said before, I do not wish to be dogmatic, and assert that any attempt along the " Newtonian " pattern is bound to fail a the present stage. Theoretical research, after all, is a field in which everybody should feel free to try any path he likes, since the risk is almost entirely his own. Only by trying in many different directions, can we be reasonably sure that some important avenue of progress will not be missed.

Now let me come back for a moment to the part of this Conference, which was more strictly related to the work of Mendeleev. In the talks by Professors Spitzin and Segré, we learned about the considerable efforts which have been made, and which are still going on, in order to fill the last remaining gaps in the Periodic System of elements. There are several reasons why this work is important, amongst others, of course, the *nuclear* properties of the new elements are often of considerable importance. But even from the point of view of ordinary physics and chemistry, we were reminded of the fact, that neither the Periodic Law itself, nor the deeper understanding of it which was attained through Bohr orbits and later Quantum Mechanics, are able to predict chemical properties with any certainty. Heavy atoms are just too complicated for us to be able to predict their properties accurately, although we think we have the right equations. Some of the differences of opinion which can easily arise on such matters were illustrated in the talk by Professor Haissinsky and in the discussion following it. At any rate, only the actual production of the unstable elements can tell us exactly what their properties are. Professor Segré in his talk engaged in some interesting speculations on the possibility of producing elements considerably heavier than those already known (1). It was also pointed out by Professor Wataghin, that according to results obtained by Fowler, very heavy elements seem to be present in cosmic rays. Conceivably, cosmic rays could become a source of information on these elements.

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(1) At this point some slides, kindly lent to the author by Professor Segré were shown; see Segré's talk in these proceedings.

The predominantly chemical part of the session in Turin was concluded with an interesting talk by Professor Goldansky, which was partly concerned with the quite unusual chemistry of positrons bound in various substances. This formed a natural link to the atomic physics half of the session, which I shall now review briefly.

Professor Weisskopf's talk has been mentioned already. It gave us a broad panorama not only of atomic physics, but also of nuclear and high energy physics; three very different subjects, but strongly related to each other. Even more remarkably, the speaker could have claimed substantial personal contributions to all three. On atomic physics, I still have to mention two interesting contributions. Professor Wheeler proved to us, that one can still say something new about electron orbits in atoms. Starting from the empirical observation that the energy of electronic orbits in a certain approximation and over a certain range is governed by the quantum-number combination $n_r + 2l$, and using numerical calculations by R. Power, Wheeler showed that a simple and intuitive interpretation of this fact can be given in terms of a characteristic shape of the electron orbit such that the periods associated with the azimuthal and radial motions are exactly in the ratio 2 : 1. The talk by Mrs. C. Moore Sitterly was a salutary reminder to some of us of the fact that spectroscopy is still very much alive, not only because of the needs of astrophysics, which continually demands new data on highly ionized atoms and other difficult-to-obtain spectra (Mrs. Sitterly gave some fascinating examples) but also because the work of understanding more an more complicated spectra (of which Racah's pioneering work remains as an outstanding example) still goes on actively, sometimes with striking and unexpected results.

While atomic physics has reached, to a large extent, the " Newtonian " stage, the same cannot be said of nuclear physics. In the part of this Conference devoted to that subject it became apparent that work in this field usually proceeds along a direction, which may be described as a combination of the two approaches described by Gell-Mann. It is hardly necessary to recall, that we do not possess an accurate " Schrödinger Equation " for the internal dynamics of a nucleus. Nevertheless, we heard in Turin that even here quite sophisticated mathematical techniques are often used. Professor Elliot showed how group-theory methods (following a pattern initiated by Racah) can be used to identify and classify nuclear levels, while Verde described a new elegant technique to obtain manageable and exact espressions for representation matrices of certain groups, and various coefficients related to Kronecker products. Unlike other more common methods, this technique also applies to non-compact groups, a vast subject, of profound intrinsic mathematical interest, and according

to some physicists, potentially very important in elementary particle physics also.

The last talk in Turin was given by Professor Bogolubov, who summarised in a masterful way the process by which certain refined mathematical techniques, originally developed in quantum field theory, have become an extremely useful tool in such diverse topics as solid state theory (superconductivity), superfluids and finally nuclear matter and nuclear states.

I have reserved a somewhat longer space for the talk by Professor Talmi, because it deals with periodic properties of atomic nuclei, which seem to fit the general topic of this Conference in an especially nice way. The question examined by Talmi is the following. How close is the analogy between the behavior of nuclei and that of atoms, in the neighborhood of magic numbers? As is well known, the ionization energy of atoms, plotted vs the atomic number $Z$, exhibits very sharp and characteristic maxima corresponding to closed shells. In order to demonstrate the existence of nuclear shell structure, physicists have used similar plots, for example of the energy required to remove a neutron, plotted versus the neutron number $N = A - Z$. Professor Talmi, however, warned us against the common misconception, that magic nuclei are very tightly bound. He showed, in fact, that *a*) the plots, as usually exhibited, are manipulated in such a way as to exhit the magic shell effect most clearly (a legitimate purpose) but are misleading to the unsuspecting eye, and in fact *b*) the unvarnished data on separation energies do not show any particularly large value at the magic numbers. Finally *c*) Professor Talmi showed that the behavior of binding energies near a closed shell can be understood and described quite adequately by means of a three-parameter formula which has a sound theoretical basis in Racah's seniority scheme (2).

Coming now to the part of the meeting, that was devoted to elementary particles, I shall review briefly some of the obvious trends, bearing in mind Gell-Mann's advice, which was especially aimed at this part of physics. I shall also bear in mind an opinion expressed by Professor Michel, according to which modern mathematics is a language, which (contrary to the traditional view) quite often deals with qualitative relationships. It is clear, at any rate, that what strong interaction theorists mean by " dynamics of strong interactions " is not a deductive " Newtonian " scheme, but rather a mixture of moderately sophisticated mathematical ideas with much guesswork, phenomenological fitting and other

(2) Some further details which were given in the talk, seem unnecessary here; the reader is referred to Talmi's report for further data.

ingredients. Please notice that I do not use these words in a deprecatory sense, but rather to point out that this work is not too far from the kind of effort Gell-Mann would like to encourage. I am thinking, for example, of the very interesting and spirited defense of the idea of duality and of Veneziano's particular brand of Reggeology we heard yesterday from Professor Fubini. In a rather different direction we heard from Professor Regge, how the study of rather difficult questions related to analyticity can pave the road to further progress on strong interactions. And still from another side sophisticated group-theory notions have been applied to the problem, as for esample in the work of Michel and Radicati. Since time is running out, and since the remaining talks I should mention are still fresh in your memory, I shall merely record that the last part of our discussions was also concerned, as it should be, with the weak and electromagnetic interactions of elementary particles. In all these subjects we found a varying mixture of straight deductive reasoning and inductive phenomenological efforts to describe a world, which has already revealed to us its extraordinary richness, even though so much of it is still hidden by the clouds of our ignorance.

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Ben Sen